KONINKLIJKE AKADEMIE VAN WETENSCHAPPEN
TE AMSTERDAM.

PROCEEDINGS

VOLUME XXIII

No. 1.

President: Prof. H. A. LORENTZ.
Secretary: Prof. P. ZEEMAN.

(Translated from: "Verslag van de gewone vergaderingen der Wis- en Natuurkundige Afdeeling," Vol. XXVIII and XXIX).

CONTENTS.

GUSTAV STIASNY: "Ueber westindische Tornarien nebst einer Uebersicht über die bisher bekannten tentaculaten Tornarien". (Communicated by Prof. J. BOEKE), p. 2. (Mit 2 Tafeln).
H. O. ANTONIUS: "Bemerkungen über einige Säugetierschädel von Sardinien". (Communicated by Prof. J. F. VAN BEMMELEN). p. 37.
NIL RATAN DHAR: "Catalysis — Part VII — Temperature Coefficient of Physiological processes". (Communicated by Prof. ERNST COHEN), p. 44.
ARNAUD DENJOY: "Sur une classe de fonctions admettant une dérivée seconde généralisée" p. 50.
C. B. BIEZENO, "Graphical Determination of the Moments of Transition of an Elastically Supported, Statically Indeterminate Beam". II. (Communicated by Prof. J. CARDINAAL), p. 60.
J. BÖESEKEN and CHR. VAN LOON: "On the determination of the configuration of cyclic cis and trans diols and the rearrangements of atoms and groups of atoms during chemical reactions", p. 69.
F. M. JAEGER: "On some Condensation-products of Aromatic Aldehydes and Amines", p. 74.
F. M. JAEGER and G. BERGER: "The Photochemical Decomposition of Potassium-cobaltioxalate and its Catalysis by Neutral Salts", p. 84.
F. M. JAEGER and J. H. DE BOER: "Colloidal Sulphurcompounds of Ruthenium", p. 95.
L. BOLK: "On the Index cephalicus and the absolute Dimensions of the Head of the Population of Holland", p. 103. (With one plate).
J. BRAMSON: "Experimental proof for the active dilatation of cross-striated muscle-tissue". (Communicated by Prof. G. VAN RIJNBERK), p. 111.
J. J. VAN LOGHEM: "Identity of the blood-digestive and gelatine-liquefying bacterial actions". (Communicated by Prof. C. EYKMAN), p. 115.
N. H. KOLKMEIJER: "Remark on the possible existence of binding rings in diamond". (Communicated by Prof. H. KAMERLINGH ONNES), p. 120.
F. GOUDRIAAN: "The aluminates of sodium. Equilibriums in the system Na_2O—Al_2O_3—H_2O. (Communicated by Prof. J. BÖESEKEN), p. 129.
J. TRESLING: "Derivation of a formula for the temperature dependence of the velocity constants in gas reactions from a special image of the process". (Communicated by Prof. H. A. LORENTZ), p 143.
H. I. WATERMAN and J. GROOT: "The influence of different substances on the decomposition of monoses by an alkali and on the inversion of cane sugar by hydrochloric acid". (Communicated by Prof. J. BÖESEKEN), p. 149.
P. EHRENFEST and V. TRKAL: "Deduction of the dissociation-equilibrium from the theory of quanta and a calculation of the chemical constant based on this", p. 162.
H. HULSHOF: "The osmotic pressure, regarded as a capillary phenomenon". (Communicated by Prof. H. A. LORENTZ), p. 184.
S. A. ARENDSEN HEIN: "Technical experiences in the breeding of Tenebrio molitor". (Communicated by Prof. J. W. MOLL), p. 193.

Zoology. — "*Ueber westindische Tornarien nebst einer Uebersicht über die bisher bekannten tentaculaten Tornarien*". By Dr. GUSTAV STIASNY. (Communicated by Prof. J. BOEKE). (Mit 2 Tafeln und 3 Textfiguren).

(Communicated at the meeting of June 26, 1920).

1. Das Material.

In einigen schönen Planktonproben, welche von Prof. Dr. BOEKE 1905 in *Holländisch Westindien* gesammelt und die mir von Prof. Dr. MAX WEBER zum Studium überlassen wurden, fanden sich zahlreiche Entwicklungsstadien von Enteropneusten, die in der vorliegenden Mitteilung näher besprochen werden sollen. Es handelt sich dabei nicht um neue bisher unbekannte Tornarien, sondern die in den Proben enthaltenen Enteropneustenlarven konnten mit ziemlicher Sicherheit mit Tornarien identificiert werden, die bereits in den Gewässern der Bahamas Inseln gefunden worden sind. *Aus Holländisch Westindien waren bisher Enteropneustenlarven nicht bekannt.* Die untersuchten Tornarien gehören zweierlei Species an und konnten in verschiedenen Entwicklungsstadien beobachtet werden, die zum Teil noch nicht oder nicht genau bekannt sind. So war es möglich, die Angaben in der Literatur über die Entwicklung dieser beiden Formen in mancher Hinsicht zu ergänzen. Die Etiquetten der Planktonproben tragen folgende Aufschriften:

1. Plankton 1905, Saba, West-Indië, Gough Bay, Dr. BOEKE, waarn. 37.
2. Plankton, West-Indie, 1905, Dr. BOEKE, Cove Bay, waarn. 36.
3. Plankton, 25/VII. 1905, Saba, West-Indië, Dr. BOEKE, waarn. 32.
4. Plankton, Aruba, West-Indië, Pays bank, Aug. 1905, Dr. BOEKE 0—30 vaam.

Insgesammt fanden sich über 300 Exemplare von Tornarien, darunter eine kleine, nur in wenigen Exemplaren vorhandene, und eine grosse häufige Form. Die kleinere ist identisch mit der sogenannten *Bimini-Tornaria*, die grössere mit der sogenannten *Bahamas-Tornaria* Morgans.

II. *Die westindischen Tornarien.*

a. Die Bimini Tornaria (Tornaria Weldoni).

(Tafel I).

Ueber die „Bimini Tornaria", welche ich zu Ehren ihres ersten Auffinders *Tornaria Weldoni* benenne, liegen Angaben von WELDON (1) und MORGAN (4) vor. WELDON und nach ihm MORGAN fanden diese kleine Form gemeinsam mit der grossen *Bahamas Tornaria* auf North Bimini Island, auf dem Westrande der grossen Bahamas Bank, gegenüber dem Südende von Florida. Da sie nunmehr auch bei Saba und Aruba nachgewiesen ist, dürfte sie wohl im ganzen westindischen Archipel einheimisch sein, doch ist sie ziemlich selten. WELDON beschreibt (l.c.) einige vorgeschrittene Entwicklungsstadien, die zum Teil bereits der Metamorphose angehören oder ihr unmittelbar vorausgehen, Stadien, die etwa der fig. 6 auf Taf I. entsprechen und z. T. bereits die für das erwachsene Tier so charakteristische Dreiteilung des Körpers in Rüssel-, Kragen- und Rumpfregion aufweisen. Da WELDON sich lediglich auf Abbildung und Beschreibung einiger Schnittpraeparate beschränkt und den äusseren Habitus seiner Form nur mit wenigen Worten andeutet, lässt sich nicht mit Sicherheit, wohl aber mit grosser Wahrscheinlichkeit, behaupten, dass die von ihm beschriebenen Entwicklungsstadien zur *Bimini-Tornaria* MORGAN's gehören. Er spricht nämlich von einer grossen und kleinen Form, die von MORGAN später an derselben Lokalität wiedergefunden und von diesem Forscher mit den Namen *Bahamas-* und *Bimini Tornaria* bezeichnet wurden. Auch in meinen Planktonproben kamen die beiden Larven nebeneinander vor.

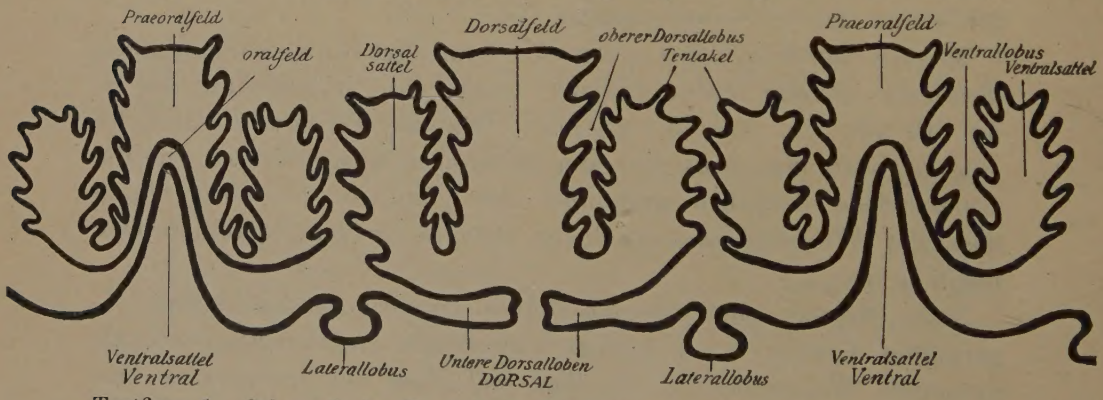
MORGAN hat einige Jahre später (4) ein jüngeres Entwicklungsstadium derselben kleinen Form genauer untersucht. Er bildet auf Taf. I. fig. 12 (4) ein Stadium ab, das etwa der *Tornaria Krohnii* des *Balanoglossus clavigerus* aus dem Mittelmeer entspricht und gibt die Unterschiede desselben gegenüber der *Bahamas Tornaria* an, so dass die Wiedererkennung dieser Species in den Planktonproben möglich war.

Nach MORGAN sind für die Bimini Tornaria charakteristisch: 1. geringere Grösse, 2. ein kleiner Unterschied im Verlaufe des longitudinalen Wimperbandes, 3. Bau und Zahl der Tentakel, 4. Bau der Apicalplatte, 5. die dem Darm anliegenden Coelome. Vergleiche darüber die Ausführungen auf S. 28/29, sowie die Synopsis auf S. 31

Während MORGAN nur ein einziges Exemplar zur Verfügung stand, bilden die von Prof. BOEKE gesammelten Exemplare eine Serie verschiedener Entwicklungsstadien, einen Ausschnitt aus der Entwicklung

eines noch nicht festgestellten Enteropneusten. Das in Fig. 4 auf Taf. I dargestellte Stadium stellt den Höhepunkt larvaler Entwicklung dar, indem es alle typischen Larvencharaktere in voller Entfaltung zeigt. Es entspricht etwa einem älteren *Tornaria Krohnii* Stadium des *Balanoglossus clavigerus* aus dem Mittelmeere und ist etwa gleich alt mit dem von MORGAN abgebildeten Stadium (Taf. I. fig. 12, 4). Dieses und die in Fig. 1—3, Taf. 1, dargestellten jüngeren Stadien gehören jener Periode der Larvenentwicklung an, die ich in meinen Arbeiten (13, 14, 15) als Periode der progressiven Entwicklung bezeichnet habe, während Stadium 5 bereits der regressiven Entwicklung, das Stadium 6 der Metamorphose angehört. In den erwähnten Arbeiten habe ich ausgeführt, dass die erstere Periode charakterisiert ist, durch continuirliche Zunahme der Körpergrösse und des Blastocoels, durch Reduction des specifischen Gewichtes, Durchsichtigkeit und fortschreitende Ausbildung des Wimperkranzes, Coeloms und Herzblase; die 2. Periode, in welcher keinerlei neue Organe angelegt werden, gekennzeichnet durch Grössenabnahme, zunehmende Undurchsichtigkeit, Reduction des Blastocoels, Zunahme des specifischen Gewichtes bis zur Aufgabe der pelagischen Lebensweise, und zum Eintritt der Metamorphose.

In der unter (15) erwähnten Arbeit habe ich in Textfig. C. auf Seite 263 ein Schema des Verlaufes des longitudinalen Wimperkranzes für die *Tornaria Krohnii* aus dem Mittelmeer gegeben. Ich gebe in Textfigur 1 ein gleiches Schema des entsprechenden Stadiums der Bimini-Tornaria. Ein Vergleich der beiden Schemata, so wie mit dem in Textfig. 2 dargestellten zeigt augenfällig die Unterschiede.



Textfigur 1. Schematische Darstellung des Verlaufes des longitudinalen Wimperbandes der ausgebildeten *Tornaria Weldoni*.

An Hand dieses Schemas lässt sich mit Hilfe der SPENGEL'schen Nomenclatur (3) der Verlauf der longitudinalen Wimperschnur der *Tornaria Weldoni* (Bimini Tornaria) kurz charakterisieren:

1. Prae- und Postoralfeld ziemlich breit, breiter als die Sättel. Loben verhältnismässig schmal.

2. 4—6 Tentakel (tentakelartig ausgebildete „secundäre Loben" an jedem der oberen Dorsalloben, so bezeichnet nach dem Vorgange SPENGELS bei *Tornaria Grenacheri* (3); eigentlich sind es die Dorsalsättel, welche die Tentakel tragen. Vergl. darüber meine Ausführungen auf p. 15/16). Die Tentakel sind kurz und breit, mehr stummelförmig,

3. Oralfeld schmal, stark gekrümmt, Ventralsattel hoch.

4. Untere Dorsalloben sehr lang und schmal, mit fast parallel verlaufenden Wimperschnüren, die dorsal fast zusammenstossen, ohne Tentakel.

5. Lateralloben tief, mit schmaler Oeffnung, ohne Tentakel.

6. An der Scheitelplatte legen sich prae- und postorale Wimperkränze parallel aneinander und verschmelzen.

Von den übrigen Merkmalen sei hier noch hervorgehoben, dass das Analfeld stark vorgewölbt, der circuläre primäre Wimperkranz kräftig entwickelt, der secundäre Wimperkranz rings um den Anus schwach ausgebildet ist und dass die Coelome dem Darm anliegen. Betrachten wir nun die einzelnen Entwicklungsstadien etwas genauer.

Tafel I, Fig. 1. Dorsalansicht eines Stadiums der progressiven Entwicklung (etwa einem etwas vorgeschrittenen *Tornaria Müller*i-Stadium (13, 14, 15) vergleichbar). Dorsalfeld breit, Dorsalloben mit je 3 breiten tentakelartigen secundären Loben, weitere in Ausbildung begriffen; untere Dorsalloben sehr lang und schmal. Links oberhalb des primären circulären Wimperkranzes der eine Laterallobus (der andere ist verdeckt), secundärer circulärer Wimperring ganz schwach. Analfeld mässig vorgewölbt. Im Innern: Mitteldarm cylindrisch, Enddarm kurz, kegelförmig. Eichelcoelom geräumig. (Eichelporus und Herzblase nicht beobachtet). Das eine der beiden Rumpfcoelome als rundliches Bläschen zwischen Mittel- und Enddarm.

Fig. 2. Ansicht schräg von oben eines etwa gleichaltrigen Stadiums mit 3 kurzen Tentakeln an den Dorsalloben und weiteren in Ausbildung begriffenen. Am Apex legen sich prae- und postorale Wimperkränze parallel an einander und verschmelzen. Lateralloben tief, Ventralband breit. Im Innern: Ein Coelomsäckchen als breite Platte dem Mitteldarm anliegend, an der Grenze zwischen Mittel- und Enddarm.

Fig. 3. Oralansicht eines etwas älteren Stadiums, das noch der progressiven Entwicklung angehört. Etwas grösser als das vorhergehende. Der longitudinale Wimperkranz wieder etwas complicierter, mit 4 Tentakeln an den Dorsalloben. Sehr deutlich das schmale

hufeisenförmige Oralfeld mit der trichterförmigen Mundöffnung und der hohe schlanke Ventralsattel zu sehen. Ventralband breit mit beiderseitigen tiefen Lateralloben. Im Innern: der 3 teilige Darm. Dem Mitteldarm liegt das plattenförmige Rumpfcoelom [1]) an, das denselben zu umwachsen beginnt. Unterhalb der Apicalplatte der glashelle Strang, an dem das Eichelcoelom befestigt ist.

Fig. 4. stellt die typische Tornaria Weldoni in ihrer vollen Entwicklung dar, mit allen Larvencharakteren ausgestattet, den Höhepunkt der Larvenentwicklung. (Dorsalansicht). Die Larve hat das Maximum der Körpergrösse, ca $2^1/_2$ m.m., erreicht. Der Verlauf des longitudinalen Wimperkranzes hat durch Ausbildung von 6 Tentakeln an jedem Dorsallobus, sowie durch die tiefen Lateralloben den höchsten Grad von Complicierthеit erlangt. Untere Dorsalloben sehr lang und schmal. Scheitelplatte entsteht durch Verschmelzung der sich parallel aneinanderlegenden prae- und postoralen Wimperkränze. Circulärer Wimperkranz breit und kräftig, secundärer Wimperkring ganz fein und schmal.

Im Innern: Zu beiden Seiten des Mitteldarmes 2 Paare von Coelomsäckchen als längliche oder rundliche Bläschen, dem Darm angelagert. Die mehr dem Enddarm zu gelegenen die Rumpfcoelome, die gegen die Scheitelplatte zu liegenden (in der Abbildung von den Tentakeln etwas verdeckt) die Kragencoelome. Das Eichelcoelom als langer schmaler kegelförmiger Sack, dem Mitteldarm aufliegend mündet durch den Eichelporus in der Mitte des Dorsalfeldes nach aussen. Durch einen ziemlich dicken Strang mit dem Apex verbunden. Herzblase nicht beobachtet.

Dieses Stadium entspricht dem von Morgan in seiner Figur 12 dargestellten, das eine Seitenansicht darstellt. Es ist das „*Tornaria Krohnii-Stadium*" der *Tornaria Weldoni.*

Fig 5. stellt ein Stadium dar, das bereits der regressiven Entwicklung angehört. Es ist gekennzeichnet durch geringere Körpergrösse gedrungenere Gestalt, geringere Durchsichtigkeit, Rückbildung der tentakelartigen Bildungen. Es sind deren jetzt nur mehr drei an jedem Dorsallobus vorhanden. Dieses Stadium ist dunkler, undurchsichtiger als das sonst ähnliche in fig. 1 abgebildete Stadium der progressiven Entwicklung, zeigt jedoch das Analfeld stärker vorgewölbt, kegelförmig ausgebildet, die Lateralloben sind nicht mehr so tief, der circuläre Wimperring ist breiter, der secundäre circuläre Wimperring ist geschwunden. Im Innern das mächtig entwickelte Eichelcoelom, das dem Darm aufgelagert ist und rechts ausmündet.

---

[1]) Nach Spengel vielleicht richtiger als „Kragen-Rumpfcoelom" zu bezeichnen.

Die Coelome konnten an diesen undurchsichtigen Entwicklungsstadien nicht mit Sicherheit beobachtet werden.

Fig. 6 zeigt ein Stadium nach der Metamorphose. Es ist noch viel kleiner als das vorige, misst circa $1^1/_2$ mm. und ist fast undurchsichtig. Der Körper zerfällt bereits in die 3 für das erwachsene Tier so charakteristischen Teile: Rüssel-, Kragen, Rumpfregion. Der keulenförmige Rüssel ist durch eine tiefe Ringfurche von der Kragenregion abgesetzt.

Die Kragenregion ist sehr breit und trägt in ihrer Mitte den in Rückbildung begriffenen circulären Wimperkranz. Das Analfeld ist wie im vorhergehenden Stadium kegelförmig vorgewölbt.

Der Tentakelapparat des longitudinalen Wimperkranzes, die Lateralloben etc. ist bereits ganz geschwunden.

Im Inneren kann man, wenn man das Objekt zwischen Deckglas und Objektträger mit der Nadel etwas quetscht, im Rüssel das riesig grosse Eichelcoelom sehen, das fast den ganzen Innerraum des Rüssels ausfüllt. Auch die Contour des Mittel- und Enddarms tritt noch einigermassen hervor.

Da mir nur wenige in Formol conservierte Exemplare zur Verfügung standen und es unter den gegenwärtigen Verhältnissen mir nicht möglich ist, Schnittpraeparate anzufertigen, waren der Untersuchung von vorneherein enge Grenzen gezogen. So musste auf die Feststellung der Art und Weise der Entstehung des Coeloms, des Herzens etc. verzichtet werden, auch wurde in die Abbildungen nur das eingezeichnet, was tatsächlich beobachtet werden konnte, ohne Ergänzungen nach Schnittpraeparaten und ohne zu schematisieren.

Auch die vorliegenden Stadien stellen keine geschlossene Reihe von Entwicklungsstadien dar. So fehlt das wichtige „eingekerbte Stadium", das ich bei *Balanoglossus clavigerus* beschrieben habe, und das seinen Platz zwischen dem in fig. 5 und 6 abgebildeten Stadien finden müsste (14,15).

Da aber von dieser Form mit Sicherheit nur das einzige von Morgan abgebildete und geschilderte Stadium bekannt ist, glaube ich doch, dass diese kurzen Angaben einen kleinen Fortschritt in der Kenntnis der Entwicklung dieser Form bedeuten.

Zum Schlusse ergibt sich natürlich die Frage, zu welchem adulten Tiere die *Tornaria Weldoni* gehört. Weldon und Morgan konnten natürlich nichts sicheres darüber aussagen. Auch zur Zeit ist dies noch nicht möglich, aber eine Vermutung lässt sich doch äussern.

Spengel (3) hat auf Grund von Material, das er von Weldon von den Bahamas erhielt, einen Enteropneusten beschrieben, den er *Ptychodera* (*Chlamydothorax*) *bahamensis* nannte. Es ist dies eine auffallend kleine Form von ca $7^1/_2$ cm Länge, von der gleichen Lokalität stammend wie die *Bimini Tornaria*, die ja auch sehr klein ist. Ich halte es daher für nicht ausgeschlossen, dass *Ptychodera bahamensis* Spengel die adulte Form der *Tornaria Weldoni* darstellt. Mit Sicherheit wird sich dies natürlich erst dann feststellen lassen, wenn aus den Eiern von *Ptychodera bahamensis die Tornaria Weldoni* gezüchtet worden.

b. Die Bahamas Tornaria (*Tornaria Morgani*).
(Tafel II).

Weldon (1) fand vorgeschrittene Entwicklungstadien einer grossen tentaculaten Tornaria bei Nassau, New Providence, Bahamas Bank, über welche er nur einige ganz beiläufige Bemerkungen macht. Morgan (2) beschrieb einige Jahre später unter der Bezeichnung „*Nassau Tornaria*" Entwicklungsstadien einer von der gleichen Lokalität stammenden, mit derjenigen Weldons offenbar identischen Tornaria mit langen Tentakeln, von der er Detailschilderungen des Verlaufs des dorsalen Wimperbandes, des Tentakelapparates und der Scheitelplatte gibt (2, Taf XXIV, fig. 10—12). Die Coelome wurden dabei nicht beobachtet. Die wichtigsten Angaben über die „*Bahamas Tornaria*" sind in seiner grossen Arbeit (4) enthalten, in welcher er einen grossen Teil der Entwicklung und Metamorphose derselben tentaculaten Tornaria bis zur Umwandlung in das benthonische Tier beschreibt. Das Material für seine Untersuchung fand Morgan in den Gewässern von Bimini-Island, Bahamas Bank (s. o. p. 2) zugleich mit der kleinen *Tornaria Weldoni*. Seine Beschreibung passt so genau auf die mir vorliegenden grossen Tornarien von Aruba und Saba, dass an der Identität beider Formen, trotz geringer Abweichungen, kein Zweifel sein kann. Es ist also wohl auch anzunehmen, dass diese von mir als „*Tornaria Morgani*" bezeichnete Tornaria im ganzen westindischen Archipel verbreitet ist. Die Angaben Morgans finden bei der Besprechung der einzelnen Organsysteme ihre gebührende Berücksichtigung.

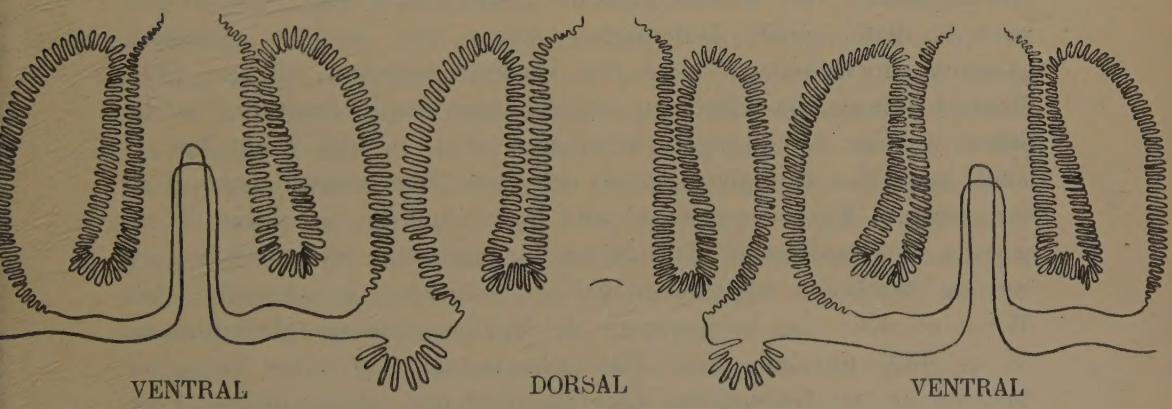
Wie von der *Tornaria Weldoni* liegt auch von der *Tornaria Morgani*, der grossen Bahamas Tornaria, eine Reihe von Entwicklungsstadien vor, die einen Ausschnitt aus der Entwicklung darstellen, umfassend die *T. Morgani* in ihrer höchsten Entwicklung (etwa dem *Tornaria Krohnii*-Stadium entsprechend) bis zum sogenannten „eingekerbten" Stadium. Die Serie umfasst gerade jene Stadien, die

zwischen den MORGAN'schen Stadien III und IV liegen (Taf. I, fig. 3 u. 4, 4) und von dem genannten Forscher nur ganz nebenbei beschrieben wurden, so dass sie eine Ergänzung zu denselben darstellt.

Infolge der Grössenabnahme, zunehmender Undurchsichtigkeit, Schwindens der Tentakel, und immer stärkerer Ausbildung der Coelome gehören die meisten Stadien mit Ausnahme des 1. Stadiums (Taf. II, fig. 7, 8), das den Höhepunkt der pelagischen Entwicklung und die typisch ausgebildete *Tornaria Morgani* mit allen Larvencharakteren zeigt, jener Periode der Entwicklung an, die ich in meinen Studien über die Entwicklung des *Balanoglossus clavigerus* (14, 15), vom morphologischen Standpunkte aus als *„regressiv"* bezeichnet habe.

Bevor ich auf die Besprechung der einzelnen Stadien näher eingehe, sei bemerkt, dass das mir vorliegende Material in Formol conserviert, daher — bei meist vortrefflicher Erhaltung — doch mehr oder minder deformiert war. Daher die etwas unregelmässige Form der Kragenregion in fig. 7 u. 8. auf Taf. II. Es wurde dabei, wie bei den übrigen Figuren, auf naturgetreue Darstellung Wert gelegt und möglichst jener von SPENGEL (9, p. 123) beobachtete Vorgang der Schematisierung vermieden. Auch wurde in die Figuren nur das eingezeichnet, was tatsächlich gesehen wurde.

Tafel II, Fig. 7 und 8. stellen die *Tornaria Morgani* in typischer Ausbildung dar. An Hand des in Textfig. 2 dargestellten



Textfigur 2. Schematische Darstellung des Verlaufes des longitudinalen Wimperbandes der ausgebildeten *Tornaria Morgani*.

Schemas lässt sich der Verlauf des longitudinalen Wimperbandes mit seinen specifischen Eigentümlichkeiten gut erkennen:

1. Dorsale und ventrale obere Loben mit 20—25 Tentakeln besetzt [1]).
2. Ventralsattel hoch und schmal.

[1]) In dem obigen Schema wurden versehentlich zuviele Tentakel eingezeichnet.

3. Die postorale (ventrale) Wimperschnur geht beim Oesophagen apicalwärts über die praeorale (dorsale) hinaus, überschreitet also die Mittellinie in einem höheren Niveau als die erstere.

4. Kein unterer Dorsallobus vorhanden, daher das Dorsalfeld sehr breit.

5. Laterallobus mit circa 5—10 Tentakeln besetzt.

Wendet man dieses Schema auf die Figuren MORGANS (4, Taf. I, 1, 2, 3, an so findet man eine gute Uebereinstimmung, bis etwa auf die Zahl der Tentakel und die Form des Ventralsattels.

Die Höhe dieser Stadien ist circa 5—6 mm., die Breite (Durchmesser des primären circulären Wimperrings) beträgt 4—4$^1/_2$ mm., die Larve ist also etwas höher als breit, etwas grösser als die Exemplare MORGANS.

Taf. II. Fig. 7. *Seitenansicht der Tornaria morgani* [1]). Dieses Stadium wurde von MORGAN (4) so ausführlich geschildert, dass ich hier nur die Unterschiede zwischen dieser Abbildung mit derjenigen MORGANS (4, Taf. I fig. 3) besprechen will. Die Tentakel scheinen etwas länger, weniger steif zu sein. Das Analfeld ist nicht so flach, sondern deutlich vorgewölbt. Die Scheitelplatte ist meist eingezogen, daher nur angedeutet. Ihr Bau stimmt mit den Angaben MORGANS (2 und 4) sowie SPENGELS (3) bei Tornaria *Grenacheri* recht gut überein. Der wichtigste Unterschied betrifft das Coelom. Dasselbe wurde anfangs von MORGAN gänzlich übersehen (2 pag. 431) und so wird es wohl jedem Untersucher wegen der von der normalen gänzlich abweichenden Lage des Coeloms ergehen. (3, p. 432). MORGAN konnte dasselbe nur auf Schnitten nachweisen und ist es daher in seine Abbildung nicht eingezeichnet. In Fig. 7 auf Taf. II sieht man das Rumpfcoelom als schmalen lang ausgezogenen Ring den ganzen Körper umgebend und dem primären circulären Wimperring dicht anliegend. Es sind zwei ringförmige schmale Scheiben. SPENGEL beschreibt das Coelom bei *T. Grenacheri* in ganz ähnlicher Weise als sehr lang ausgezogene der Epidermis anliegende Schläuche (3, p. 432) nur mit dem Unterschiede, dass bei seiner Form die Coelome in der Gegend des Laterallobus einen langen dünnen Fortsatz nach oben entsenden, was bei *T. Morgani* nicht der Fall ist. Hier sind die Figuren Morgans (4, Taf. III, fig. 29, 30, 31) für den Vergleich von Wichtigkeit, die sämmtlich Schnittpraeparate darstellen. Alle zeigen das Rumpfcoelom in Verbindung mit dem Ektoderm unmittelbar dem circulären Wimperring anliegend „atta-

[1]) In fig. 7, 8 u. 9 ist der circuläre Wimperring nicht eingezeichnet, um das Coelom deutlicher hervortreten lassen zu können.

ched to the inner surface of the circular band", stets weit vom Darm entfernt. In fig. 29 ist auch das Kragencoelom mit dargestellt, welches ich auf meinen ungeschnittenen Exemplaren nicht auffinden konnte und das vielleicht erst etwas später zur Ausbildung gelangt. (Vergl. die Bemerkung unten auf S. 240).

Fig. 8 stellt ein anderes etwas grösseres Exemplar in Dorsalansicht dar. Scheitelplatte eingezogen, Analfeld eine ganz flache Scheibe. Etwas unterhalb der Mitte ist der lange schmale Ausführungsgang des „Wassersackes" sichtbar, der ziemlich tief in einer halbmondförmigen Vertiefung mündet. Oberhalb des Porus die Herzblase mit der Rüsseldrüse. Die beiden Rumpfcoelome verlaufen ganz entsprechend dem in Fig. 7 dargestellten Stadium innerhalb des circulären Wimperrings, demselben eng anliegend. Hier sieht man auch, was Morgan in Fig. 23 auf Taf. IV, Spengel in Fig. 59 Taf. 23 dargestellt hat: dass die beiderseitigen Rumpfcoelome unterhalb des Hydroporus sich einander nähern, ohne jedoch mit einander zu verschmelzen („these do not meet in the middle line"). Doch ist hier gegenüber der Beschreibung Spengels ein Unterschied, indem die Coelome bei seiner Form sich zuletzt etwas aufrichten und der linke in der Nähe des Eichelporus, der rechte in entsprechendem Abstande vom blinden Zipfel des „Wassersackes" endigt. Dagegen stimmen die Verhältnisse auf der Ventralseite, Spengels Fig. 60 Taf. 23, sehr gut, denn auch hier nähern sich in beiden Fällen die Coelome, ohne in einander überzugehen.

Stadium Fig. 9. Seitenansicht eines etwas älteren Stadiums der regressiven Entwicklung. Die Larve ist kleiner, ca $4^1/_2$—5 mm. hoch, undurchsichtiger, die Kragenregion sehr breit, wulstartig verdickt, das Analfeld ziemlich stark vorgewölbt, die Tentakel an den Loben kürzer und dicker. Im Innern der 3-teilige Darm und das dem (nicht gezeichneten) circulären Wimperring dicht anliegende ringförmige Rumpfcoelom. An der Berührungsstelle mit dem Ektoderm ist es ein wenig umgebogen, erscheint daher etwas dunkler, springt nach innen etwas vor, als ganz flache Scheibe.

Stadium Fig. 10. Dorsalansicht eines etwas älteren Stadiums als das vorhergehende. Die Epidermis ist bereits recht undurchsichtig geworden, die Tentakel sind sehr viel kürzer, nur mehr stummelförmig ausgebildet. Der „Wassersack" ist eine mächtige Blase geworden. Am Darme sind bereits in der Nähe des Oesophagus die Anlagen der ersten Kiemenspalten zu sehen. Sie treten als paarige Aussackungen der endoblastischen Darmwand auf, als halbkugelige Protuberanzen, wie von Morgan geschildert (4, p. 42). Die Coelome sind in Toto-Praeparaten fast nicht zu sehen, da sie durch den

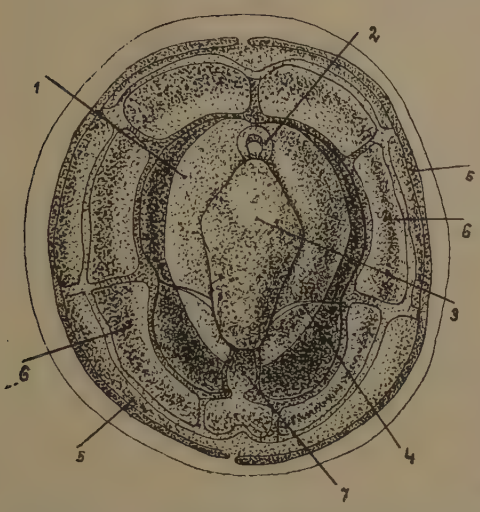
breiten circulären Wimperkranz verdeckt werden, dem sie eng anliegen. Dass sie bereits vorhanden und sehr mächtig entwickelt sind, kann man auf Zupfpraeparaten der gleichen Stadien sehr deutlich erkennen. (Vergl. Textf. 3 u. die Ausf. S. 230/231).

Stadium fig. 11. entspricht etwa dem Morgan'schen Stadium IV (4, Pl. I, fig. 4) und meinem eingekerbten Stadium (15, Taf. 6, Fig. 6 u. 7). Die Tentakel sind bereits völlig geschwunden, die Dorsal- und Ventralloben ganz glatt, die Lateralloben sind verwischt. Die Kragenregion breit, wulstartig, ähnlich, wie bei dem in fig. 9 auf Taf. II dargestellten Stadium, das Analfeld sehr stark vorgewölbt. In der Mitte des Körpers ist bereits die für dieses Stadium so charakteristische ringförmige Einschnürung oder Einkerbung zu sehen. Im Innern der Darm und der grosse Wassersack (Eichelcoelom); in der Kragenregion sind die Kragen- und Rumpfcoelome zu sehen. Man sieht in der Figur 11 oberhalb des grossen circulären Wimperrings die etwas dunkler gehaltenen Rumpfcoelome, oberhalb, d. h. in Wirklichkeit innerhalb derselben, die gleichfalls schon stark ausgebildeten Kragencoelome. Diese springen diaphragmaartig ins Innere vor, stets concentrisch den äussern Rumpfcoelomen und denselben dicht anliegend verlaufend. Besser ist dies natürlich auf Zupfpraeparaten zu sehen. (Vergl. Erläuterungen zu Textf. 3). Auf Zupfpraeparaten lassen sich in diesem bereits sehr undurchsichtigen Stadium auch 2 Paar Kiemenspaltenanlagen als halbkugelige Vorwölbungen zu beiden Seiten des Oesophagus erkennen.

Stadium fig. 12. Dieses kleinste bereits ganz undurchsichtige leicht rötlich-bräunlich gefärbte Stadium halte ich für das älteste, vorgeschrittenste. Es scheint der Metamorphose unmittelbar vorauszugehen. Vor allem fällt die sehr stark vorgewölbte Analplatte und die tiefe Ringfurche auf, ferner die in voller Auflösung befindliche longitudinale Wimperschnur der Rüsselregion. Es scheint hier ein „vollständiger Zerfall ganzer Bezirke des Hautepithels" (12) und Auflösung des longitudinalen Wimperkranzes in einzelne mehr oder minder vertikal zur Längsachse stehende Stücke stattzufinden, die stellenweise noch gewellten Verlauf zeigen (Schrumpfung?). Im Innern ist mit Mühe der Darm und die grosse Wasserblase (Eichelcoelom) zu sehen. Coelome und Kiemenspaltenanlagen sind in Totopraeparaten nicht zu erkennen.

Textf. 3 stellt ein Totalpraeparat im optischen Schnitte dar. Die undurchsichtige Epidermis des Analfeldes ist mittels feiner Nadeln abgetragen, so dass dasselbe von einem ganz durchsichtigen uhrglasförmigen Häutchen bedeckt ist, durch welches hindurch man das ganze Innere der Larve beobachten kann. Es ist ein dem Stadium 10 entsprechendes Objekt dargestellt.

Ganz peripher der grosse Wimperkranz, im Bilde nur angedeutet. Ihm anliegend die paarigen Rumpfcoelome, welche in der Sagittalachse sich nähern. Dieselben zeigen peripher jederseits einen verdickten schlauchartigen Halbring mit deutlichem dünnen Lumen, der sich nach innen zu als solide Platte fortsetzt, was der fig. 30, Taf. IV Morgans mit dem Unterschiede entspricht, dass bei Morgan gerade umgekehrt der innere Teil des Rumpfcoeloms das Lumen zeigt. Während in den jüngeren Stadien, die in Fig. 7 u. 8 dargestellt sind, nur der periphere schlauchartige Teil zu beobachten ist, finden sich bei etwas älteren Stadien, Fig. 9 u. 10, wie etwa hier, plattenförmige Fortsätze im Innere. Diese inneren Teile des Rumpfcoeloms scheinen in der Sagittalachse mit einander beiderseits zu verschmelzen, während die peripheren getrennt bleiben. Apicalwärts vom Rumpfcoelom, im Bilde innerhalb, liegen die mächtig entwickelten Kragencoelome, welche als breite diaphragmaartige Platten ausgebildet sind und vom Rumpfcoelom durch eine deutlich erkennbare schmale concentrische durchsichtige Zone getrennt sind. Sie sind in meinen Stadien riesig gross, ganz breite weit ins Innere vorspringende Scheiben, so dass es fast unbegreiflich erscheint, wieso sie von Morgan, der ganz entsprechende Stadien vor sich hatte, entweder gänzlich übersehen werden konnten oder auf den Schnitt-praeparaten (4, Taf IV Fig. 29 u. 35) nur so klein ausgebildet sind. Die beiderseitigen Kragencoelome vereinigen sich in der Sagittalachse und scheinen dort Mesenterien zu bilden, an denen sich auch die Rumpfcoelome anheften. In der Gegend des Oesophagus legen sich die Kragencoelome an den Oesophagus an. An vier Stellen, etwa den äusseren tentakeltragenden Loben entsprechend, sieht man Verdickungen im Coelom, von denen apikalwärts in manchen Fällen Fortsätze auszugehen schienen, doch war mir dies in anderen Fällen wieder



Textfigur 3. Optischer Schnitt durch ein Total-praeparat (Stadium fig. 10) von *Tornaria Morgani*. Die Larve ist so orientiert, dass die Apikalplatte zu unterst, der After zu oberst ist, sie steht also gleichsam auf dem Kopfe. 1 Wassersack, 2 Herzblase und Rüsseldrüse, 3 Darm, etwas oberhalb des Bildcentrums der After, 4 Sporne („Zügelstücke"), 5 Rumpfcoelome, 6 Kragencoelome, 7 Oesophagus.

zweifelhaft, und konnte dies mit Sicherheit nicht festgestellt werden.

Weiter ins Innere fortschreitend ist in der Abbildung das nicht mehr so geräumige Blastocoel, ziemlich dunkel gehalten, dargestellt. Es folgt das grosse muskulöse Eichelcoelom (1), dem der Darm aufliegt (3). Herzblase und Rüsseldrüse (2) deutlich zu sehen. Der dreiteilige Darm erscheint stark verkürzt, der After ganz oben, im Bilde oberhalb des Centrums, der Oesophagus in der Tiefe, in einem ziemlich scharfen Winkel abgebogen (7). Sehr deutlich sieht man hier beiderseits des Darmes, dem Wassersack aufliegend, die Zügelstücke, ‚Sporne' (4). Dieselben inserieren einerseits ziemlich nahe am Oesophagus als breite anscheinend muskulöse Bänder, *ziehen dann bogenförmig, sich immer mehr fadenförmig verdünnend, beiderseits zu einer ziemlich weit ins Innere vorspringenden verdickten Stelle des Kragencoeloms, wo sie angeheftet sind.* Diese ‚Sporne' sind auch von Morgan und Spengel beobachtet worden. Besonders bei der Spengel'schen *„Tornaria Grenacheri"* (3, Taf. 23 fig. 60) sind sie sehr stark ausgebildet. Die Insertionsstelle dieser Sporen ist nach beiden Autoren nicht sicher. Nach Spengel endigen sie beiderseits „in einem bald kleineren, bald grösseren Häufchen von Zellen".

Damit glaube ich alles geschildert zu haben, was an derartigen Totalpraeparaten zu sehen ist. Schnitte konnten vorläufig nicht gemacht werden. Es ist daher vielleicht nicht alles richtig gedeutet, was ich beobachtet habe[1]).

Hier anschliessend nur einige Bemerkungen über die *Scheitelplatte* in den Stadien 7 u. 9. Taf. II. Bei den meisten Larven ist die Scheitelplatte stark eingezogen und undeutlich, oder gar nicht zu sehen, ebenso die Augen, an denen niemals Pigment beobachtet werden konnte. In der einen oder anderen Larve konnten jedoch die Verhältnisse an der Scheitelplatte, Verlauf der Wimperschnüre etc., gut erkannt werden. Im allgemeinen entspricht die Darstellung und Beschreibung Morgans in seinen beiden Arbeiten (2 u. 4) sehr gut. Besonders hebe ich hier die fig. 10 in Morgans erster Arbeit (2) hervor, in welcher Abbildung jedoch leider die Augen nicht eingezeichnet sind. Auch die Angaben Spengels (3) über die Scheitelplatte seiner als *„Tornaria Grenacheri"* bezeichneten Form zeigen durch ihre Uebereinstimmung die nahe Verwandschaft derselben mit *Tornaria Morgani.* Ich füge nur hinzu, dass im Centrum der Apikalplatte ein kleiner dunklerer Fleck zu sehen ist, innerhalb dessen sich eine kleine lichte Grube („Wimperorgan Spengels? 3, p. 394) befindet.

[1]) Zusatz bei der Korrektur. Seitdem dies geschrieben wurde, bin ich in den Besitz vorzüglicher Schnittpraeparate durch diese Stadien gelangt. Ich behalte mir vor, darauf bei anderer Gelegenheit zurückzukommen.

Quer über die Apikalplatte verläuft eine seichte Rinne. Die breite Apikalplatte selbst hat etwa die Form eines Rechtecks, dessen Längsseiten von den parallel zu einander verlaufenden tentakellosen Wimperschnüren eingenommen werden. Die prae- u. postoralen Wimperschnüre scheinen nicht auseinander zu fallen (Morgan 2, p. 11), sondern, dort, wo in der Mitte des Rechtecks die quere zu den kurzen Seiten des Rechtecks parallele Rinne verläuft, gehen die beiderseitigen Wimperschnüre in einander über, deren Tentakel gegen den Apex zu immer kleiner geworden und hier endlich ganz geschwunden sind.

Zum Schlusse ergibt sich naturgemäss auch hier die Frage: *Zu welchem adulten Enteropneusten gehört die Tornaria Morgani?* Leider lässt sich dieselbe vorläufig ebensowenig mit Sicherheit beantworten, als dies bei der *Tornaria Weldoni* und bei allen übrigen tentaculaten Tornarien der Fall ist. Weldon und Morgan sagen diesbezüglich nichts. Willey (6) spricht anlässlich der Beschreibung seiner neuen species *Ptychodera bimiiniensis* auf p. 288 folgende Ansicht aus: „This is presumably the species whose *Tornaria*-development was described by Morgan", wohl deshalb, weil diese Enteropneustenform von der gleichen Lokalität stammt. Ein weiterer Beweis für seine Behauptung wird von Willey nicht beigebracht, doch ist seine Annahme wohl richtig. Mit voller Sicherheit wird sich die Zusammengehörigkeit der *Tornaria Morgani* mit *Ptychodera bimiiniensis* natürlich erst nach Züchtung dieser Larve aus deren Eiern behaupten lassen. Am Schlusse seiner Beschreibung fügt Willey, (6, p. 294) noch hinzu: „As at least two kinds of *Tornaria* have been recorded from the West Indies it is important to note that so far as known all the Enteropneusta inhabiting the shores of these islands belong to the family of the *Ptychoderidae*."

III. *Kritische Uebersicht über die bisher bekannten tentaculaten Tornarien.*

A. Kritik der Species.

Im Anschlusse an diese Darstellung gebe ich im folgenden eine *Revision der bisher beschriebenen tentaculaten Tornarien.* Spengel hat, da sich unter den verschiedenen, in seiner grossen Monographie fälschlich zu einer einzigen Species „*Tornaria Grenacheri*" zusammengezogenen Tornarien eine grössere Anzahl wohl charakterisierter Arten erkennen lassen, eine Uebersicht derselben für nötig gehalten, eine solche in Aussicht gestellt, doch ist dieselbe bis nun nicht erschienen (9). Willey schreibt mit vollem Rechte (6, p. 185): „No doubt the differences between the Tornariae of some species are very

trifling, but it is a great mistake to imagine that all tentaculated Tornariae belong to one species".

Es ist ganz richtig, wenn SPENGEL schreibt (9, p. 127.), dass „weder die besondere Ausbildung der Tentakel noch ihre Zahl zur Charakterisierung der meisten tentaculaten Tornarienformen brauchbare Merkmale zu bieten scheint", doch sind es nicht nur „Eigentümlichkeiten gewisser Loben, an die sich vorzugsweise die Unterschiede knüpfen", sondern, wie ich hinzufüge auch *eine ganze Reihe anderer Merkmale* wie z. B. die Grösse, Beschaffenheit des Analfeldes, Bau der Scheitelplatte, Augen, Pigment, Sporne, vor allem jedoch die *Lage und Entstehungsweise des Coeloms,* (Vergl. die Synopsis der tentaculaten Tornarien S. 249), die zu einer genaueren Charakterisierung der verschiedenen Tornarien dienen können.

Bezüglich des longitudinalen Wimperbandes der tentaculaten Tornarien möchte ich nur bemerken, dass der Verlauf desselben im Prinzipe, trotz der grossen Complicierтheit gegenüber den nicht tentaculaten, doch im grossen und ganzen der gleiche ist, wie bei den letzteren. Nie ist das longitudinale Wimperband unterbrochen, sondern stets continuirlich. Man kann wohl sagen, dass soferne nach Angabe WILLEYS bei der Tornaria von New Britain (*Tornaria* WILLEYI) die Wimperschnur eine Unterbrechnung zeigen soll, dies höchstwahrscheinlich auf einen Beobachtungsfehler dieser höchst schwierig feststellbaren Verhältnisse zurück zu führen ist. Es gilt also ganz im allgemeinen das Schema des Verlaufs der longitudinalen Wimperschnur auch für alle tentaculaten Tornarien, wie ich dasselbe in meiner Arbeit (15) über die Entwicklung des *Balanoglossus clavigerus* für das *Tornaria Krohnii-Stadium* dieses Enteropneusten gegeben habe. (15, p. 263., Textf. C.). Es lässt sich daher auch in allen Fällen die SPENGELsche Nomenclatur (Loben, Sättel, Ventralband etc.) gut und zweckmässig anwenden. Natürlich hat jedoch jede einzelne Tornariaspecies einen ihr eigentümlichen Verlauf der longitudinalen Wimperschnur mit specifischen Unterschieden, die sich jedoch alle auf das gemeinsame Schema zwanglos zurückführen lassen. (Vergl. Textf. 1 u. 2 mit der genannten Abbildung).

Bezüglich der „Tentakel" sei noch eine mehr nebensächliche Bemerkung gestattet, da hier die SPENGELsche Nomenclatur zu Missverständnissen Anlass geben könnte. SPENGEL bezeichnet die Fortsätze des Oralfeldes in die benachbarten Felder mit einem der Beschreibung der Ammoniten entnommenen Ausdruck als „Loben", die in das Oralfeld hineinragenden Fortsätze der anderen Felder als „Sättel" (3, p. 373). Bei der Beschreibung seiner „*Tornaria grenacheri*" (3, p. 379/89) schreibt SPENGEL: „Die Complicierтheit des Wimperappa-

rates beruht auf der Entwicklung von je 25—30 und mehr secundärer Loben . . . Alle diese secundären Loben sind bei der ausgebildeten Larve sehr lang und schmal und haben ganz das Aussehen von kleinen Tentakeln, wie sie denn auch von WELDON als solche beschrieben worden sind". Im Sibogawerk (9, p. 124) schreibt dieser Forscher: „Bei allen (tentaculaten Tornarien) sind bekanntlich die scheinbaren Tentakel nichts als zahlreiche enge und sehr tiefe Buchten der im übrigen ihre normale Anordnung zeigenden Wimperschnüre". — Danach wären die Tentakel als „secundäre Loben" aufzufassen, also als Nebenverzweigungen der Fortsätze des Oralfeldes in die anderen Felder, die von entsprechenden Windungen der Wimperschnüre begleitet sind, also die tiefliegenden Buchten der Loben des Oralfeldes, zwischen den hochliegenden Teilen der Sättel. Von RITTER und MORGAN wird übereinstimmend angegeben, dass die Tentakel ziemlich stark von der Oberfläche wegstehen „hanging freely like a fringe from the surface of the larva", (4, p. 429) was ich nur bestätigen kann. SPENGEL selbst (3, p. 380) erwähnt die Aehnlichkeit der tentaculaten Tornarien mit einer Rippenqualle. Auch kommt den Tentakeln mehr oder minder Bewegungsfähigkeit zu (8, p. 175). *Die tiefliegenden Fortsätze des Oralfeldes, die Buchten der Loben* (SPENGEL) *können doch nicht von der Oberfläche wegstehen oder fransenartig herabhängen und sich bewegen. Die Tentakel sind eben nicht Ausbuchtungen der Loben, sondern Ausbuchtungen der Sättel,* denn nach ZITTEL's Handbuch [1]) sind die vorspringenden Teile die „Sättel", die zurückgebogenen Buchten die „Loben".

In der folgenden Besprechung wurden die meisten Tornarien mit *neuen Namen* bezeichnet. Der Vorschlag SPENGELS (3), die Tornarien mit dem Namen jenes Autors zu benennen, der sie zuerst beschrieben hat, erweist sich als nicht immer durchführbar, da z. B. SPENGEL selbst und WELDON mehrere Tornarien beschrieben haben. Es wurden daher die verschiedenen Species mit den Namen jener Autoren belegt, die an ihrer *Auffindung oder Beschreibung* einen wesentlichen Anteil haben.

Tornaria Grenacheri SPENGEL.

Unter dem Namen „*Tornaria grenacheri*" beschreibt SPENGEL (3, p. 378 ff.) eine Tornaria, die Professor GRENACHER bei den Cap Verdischen Inseln gesammelt hat und hält dieselbe für identisch mit anderen Tornaria-Exemplaren, die von CHIERCHIA auf der Fahrt des

[1]) ZITTEL KARL A., Handbuch der Palaeontologie I. Abth. Palaeozoologie II. Bd. Mollusca und Arthropoda.

„Vettor Pisani" im Stillen Ozean, zwischen den Sandwich- und den Marshall-Inseln gesammelt wurden.

Auch die von Weldon, Brooks und Morgan bei den Bahamas gefundene Form hält Spengel mit den genannten für identisch, sowie eine von Driesch und Herbst bei Ceylon nachgewiesene Tornaria. „Sollte sich wirklich die völlige Identität dieser sämmtlichen Tornarien erweisen, so würde denselben eine, wenn ich so sagen darf, circumterrane Verbreitung zukommen."

Dieser von Spengel geäusserte Zweifel an der Identität der genannten Tornarien verschiedener Provenienz erweist sich nur zu begründet. Willey (6, p. 285) bemerkt dazu, das Spengel unter dem Namen „*T. Grenacheri*" Tornarien vereinigt, die sicher nicht identisch sind.

Im Sibogawerk gibt Spengel selbst zu (9, p. 124), dass er „die tentakulaten Tornarien fälschlich zu einer einzigen Form, der *T. Grenacheri*, zusammengezogen hat, während sich einige wohl charakterisierte Arten unter ihnen erkennen lassen".

Tatsächlich ergibt eine Prüfung seiner Darstellung in seiner grossen Monographie (l.c.), dass dieser Forscher tatsächlich hier mindestens zwei verschiedene Tornarien unter dem Namen „T. Grenacheri" vereinigt hat.

Vor allem besteht zwischen der Tornaria Grenachers und derjenigen Chierchias ein beträchtlicher Grössenunterschied. Die grössten von Grenacher beobachteten Exemplare, erreichen 5—9 m.m. Höhe, das grösste von Chierchia gesammelte dagegen nur 5 m.m. Höhe.

Auf Grund seiner Abbildungen (3, Taf. 22, fig. 11—13) welche nicht nach den Grenacherschen capverdischen, sondern nach den von Chierchia gesammelten pacifischen Formen gezeichnet sind, lässt sich mit Sicherheit sagen, dass die Chierchia'sche Tornaria nicht identisch ist mit der grossen *Bahamas Tornaria* Weldon's und Morgan's. Allerdings sind beide Tornarien sehr ähnlich und Willey sagt mit Recht (9, p. 285) „no doubt the differences between the Tornariae of some species are very trifling", doch hat die Chierchia'sche Tornaria ziemlich tiefe untere Dorsalloben, welche bei der Bahamas Tornaria gänzlich fehlen (was Spengel übersehen zu haben scheint), auch erreicht die letzere nicht die Grösse der ersteren. (Vergl. damit S. 249). Spengels Beschreibung lässt diesbezüglich keine Schlüsse zu, denn er spricht stets ganz allgemein über „*Tornaria Grenacheri*", da er ja alle tentaculaten Formen für identisch hält und auch nicht sagt, ob seine jeweiligen Angaben die Grenacher'sche oder Chierchia'sche Form betreffen. Nur in der Figurenerklärung von Tafel 22 erwähnt er bei Fig. 11—13 „*Tornaria Grenacheri* aus dem Stillen

Ozean, ausgebildete Form", woraus hervorgeht, dass diese Figuren die Chierchia'sche Tornaria darstellen. Auch scheint es, dass Spengel von Grenacher nur Abbildungen, keinerlei Material, von der capverdischen Tornaria erhielt, während dies bei der Tornaria Chierchias wohl der Fall war. Danach wären dann alle Detailangaben über Coelomverhältnisse, Herzblase, Darm, Wimperkranz etc., die in Spengel's Monographie verstreut sind, auf die Tornaria Chierchias und nicht auf die Grenacher'sche zu beziehen.

Auch die Angaben Spengels über die Entwicklungsstadien der „*Tornaria Grenacheri*" sind mit einiger Vorsicht aufzunehmen, denn es scheint auch hier keinem Zweifel zu unterliegen, dass er Entwicklungsstadien verschiedener Tornarien in Verbindung gebracht hat, die mit einander nichts zu tun haben.

Durch die vortreffliche Schilderung der Entwicklung der grossen *Bahamas Tornaria* durch Morgan sind die Jugendstadien dieser Form zum Teil wenigstens bekannt (4, Taf. I, Fig. 1 u. 2). Sie sehen durchaus nicht so aus wie die *Tornaria Krohnii* des Mittelmeeres, sondern haben, obwohl viel kleiner, doch schon ganz den Habitus der tentaculaten Formen mit langen fingerförmigen Tentakeln, die allerdings geringer an Zahl sind als bei den „ausgebildeten".

Spengel schreibt nun von seiner „*Tornaria Grenacheri*", dass „Professor Grenacheri einige jüngere Entwicklungsstadien seiner Larve beobachtet und gezeichnet hat, von denen eines fast genau die *Tornaria Krohnii* repraesentiert", fügt jedoch hinzu; „Es ist allerdings nicht ganz ausgeschlossen, dass dieses vermeintliche Jugendstadium der T. g. wirklich eine *Tornaria Krohnii* ist, da ja recht wohl bei S. Vincente beide Arten neben einander vorkommen können, wie bei Neapel *T. Krohnii* neben *T. Mülleri* und *T. dubia* . . . Diese Möglichkeit muss ich zugeben."

Spengel hält es also selbst für gar nicht ausgeschlossen, dass hier eine Vermengung von Entwicklungsstadien zweier verschiedener Tornarien vorliegen kann.

Eine weitere Nachprüfung dieser Spengel'schen resp. Grenacher'schen Angabe ist nicht möglich.

Wohl möglich ist aber eine kritische Untersuchung der folgenden Bemerkungen Spengels, welche die Weldon'sche *Bahamas Tornaria* betreffen.

„Dass indessen jüngere Exemplare der *T. Grenacheri* in der Gestaltung ihres Wimperapparates tatsächlich von der *T. Krohnii* kaum zu unterscheiden sind, ersehe ich aus dem reichlichen Material der ersteren Form, das Mr. Weldon mir in liebenswürdigster Weise zur Verfügung gestellt hat". Nun hat Weldon, wie aus seiner kurzen

Mitteilung (1) hervorgeht, auf den Bahamas zwei verschiedene Tornarien beobachtet, eine kleinere, welche von MORGAN später *Bimini Tornaria* genannt wurde, und eine grössere, von MORGAN als *Bahamas Tornaria* bezeichnet. Es ist also wieder unsicher, was für Entwicklungsstadien SPENGEL VON WELDON erhielt, solche von der *Bimini-* oder solche von der *Bahamas Tornaria*. WELDON beschreibt in der genannten Arbeit (1) ausschliesslich ältere Stadien, die sich schon der Metamorphose nähern, die jungen Entwicklungstadien der *Bimini Tornaria* waren zur Zeit, da SPENGEL seine Arbeit schrieb, nicht bekannt. Aus der MORGAN'schen Abbildung 4, Taf. 1, fig. 12 geht jedoch hervor, dass es sich um eine tentaculate Form mit tentakellosem Laterallobus handelt, was auch durch das mir vorliegende übereinstimmende Material bestätigt wird. Dass die jüngeren Stadien der *Bahamas Tornaria* (*T. Morgani*) ganz anders aussehen, wie *Tornaria Krohnii*, geht aus der MORGAN'schen Beschreibung deutlich hervor (4, Taf. I, fig. 1 u. 2). Die Angabe SPENGELS stimmt also weder für die eine, noch für die andre Form WELDONS. SPENGEL fährt dann fort: „Die jüngste endlich der von Herrn Prof. GRENACHER abgebildeten Larven gleicht wesentlich einer *T. Mülleri*, indem die primären Loben, mit Ausnahme der Laterallobeu, ausgebildet sind, secundäre aber noch gänzlich fehlen. Wir würden demnach im Entwicklungsgang der *T. Grenacheri* zwei Stufen erkennen, welche die Endstadien der *Tornaria Mülleri* und *Krohnii* entsprechen". Darauf wäre einzuwenden, dass von keiner einzigen tentaculaten Form mit Sicherheit ein der *T. Mülleri* entsprechendes Entwicklungsstadium bekannt ist ohne secundäre Loben, da das jüngste bekannte Entwicklungsstadium einer tentaculaten Tornaria, dasjenige von MORGAN in Fig. 2 auf Taf. I. abgebildete und genau beschriebene, bereits Tentakeln trägt.

Da also von keiner tentaculaten Tornaria ein tentakelloses der *Tornaria Mülleri* entsprechendes Stadium bekannt ist, erweist sich SPENGELS Schlussfolgerung als voreilig oder jeder Grundlage entbehrend.

Vielmehr ist anzunehmen, dass die *Tornaria Mülleri*-Stadien GRENACHERS als jüngere Stadien jener *Tornaria Krohnii* GRENACHERS, welche auf der gleichen Lokalität gefunden wurden, aufzufassen sind, die mit der *Tornaria Grenacheri* nichts gemeinsam haben, als das Vorkommen auf einer derselben Lokalität, denn nach SPENGEL selbst (3, p. 376) „durchläuft ja die *Tornaria Krohnii* ein im wesentlichen der *T. Mülleri* gleichendes Entwicklungsstadium".

Auch ist es nach den Beobachtungen MORGANS, sowie meinen eigenen, höchst wahrscheinlich, dass sowohl die *Bimini-* als auch die *Bahamas Tornaria* sehr frühzeitig den Habitus der Tentaculaten

zeigen. Von Interesse wäre es natürlich zu wissen, was für Tornarien WELDON an SPENGEL gesandt hat, denn von den Bahamas ist eine *Tornaria Krohnii* nicht bekannt. Ich komme also zum Ergebnis, dass SPENGEL unter der Bezeichnung *T. Grenacheri* mindestens zwei Formen vereinigt hat, die Entwicklungsstadien verschiedener Enteropneusten darstellen.

Die von den Capverdischen Inseln stammende „*T. Grenacheri*", die SPENGEL wohl nur nach Zeichnungen und Angaben GRENACHERS kannte, ist nicht identisch mit der Tornaria CHIERCHIAS aus dem Pacific, die SPENGEL genau untersucht hat.

Möglich ist, das die GRENACHER'sche Larve, über welche wir nun fast gar nichts wissen, da fast sämmtliche Angaben SPENGELS auf die Tornaria CHIERCHIAS zu beziehen sind — ausser einer Aehnlichkeit beider Formen — identisch ist mit der *Bahamas Tornaria Morgans.* Die räumlich so getrennten Faunengebiete der Capverden und Bahamas sind ja durch den Golfstrom in direkter Verbindung. Es würde nur die grosse Entfernung dagegen sprechen. Hier ist jedoch die Auffindung von Tornarien durch die Planktonexpedition fern vom Festlande oder Inseln im Atlantik von Interesse. HENSEN schreibt in seinem grossen Werke „Das Leben im Ozean nach Zählung seiner Bewohner" (10) auf p. 254, dass mit dem grossen Vertikalnetze eine Anzahl *Balanoglossus* Larven 300 Seemeilen östlich von Fernando und 780 Seemeilen westlich von Ascension gefangen wurden. „Dies sind Entfernungen die der Südaequatorial-Strom kaum in 40 Tagen von Ascension durchlaufen hätte und die gegen ihn von Fernando aus nicht durchmessen werden können. Auf den Stationen zwischen dem Fundort und Ascension traten diese Larven auch nicht auf". Die weitere Bemerkung HENSENS: „Die Möglichkeit, dass die Larven, die übrigens recht häufig waren, aus grossen Tiefen stammen, ist nicht abzuweisen", bezieht sich wohl nur auf die gleichzeitig mit den Balanoglossus-Larven besprochenen Echinodermenlarven, denn bisher ist von keiner einzigen Enteropneustenform, die als typische Litoraltiere gelten, Aufenthalt in der Tiefsee nachgewiesen.

Die grosse Entfernung der Fundstellen wäre also kein Hindernis. Auch ist aus meinen Arbeiten (14, 15) über die Entwicklung des *Balanoglossus* bekannt, dass die Larvenentwicklung unter normalen Verhältnissen mehrere Wochen dauert, jedoch unter abnormen, wenn die Larven durch Strömungen verschleppt werden, natürlich länger. Für die Möglichkeit der Identität der Capverdischen und grossen *Bahamas Tornaria* spricht endlich noch eine Bemerkung SPENGELS, der erwähnt, dass bei seinen vermeintlichen Jugendstadien der *T. Grenacheri* „der Wassersack schon eine bedeutende Ausdehnung erfah-

ren hat." Auch erwähnt er eine briefliche Mitteilung Grenachers an ihn, dass es Grenacher in Erstaunen gesetzt habe, dass „das Wassergefässsystem und seine Adnexe (i. c. Herzblase, Eichelkieme) bei anscheinend ziemlich gleichweit ausgebildeten Exemplaren so ungemein verschieden entwickelt sich vorfanden." Derartige Schwankungen in der Entwicklung einzelner Organe sind bei aus ihrer ursprünglichen Umgebung verschleppten Entwicklungsstadien durchaus nichts ungewöhnliches und durch den Wechsel der physikalisch-chemischen Bedingungen des Mediums leicht zu erklären.

Die Spengel'sche „*Tornaria Grenacheri*" umfasst also 1. die *Tornaria Grenachers* von den Capverdischen Inseln, 2. die von Driesch und Herbst bei Ceylon gefangenen *Tornarien*, 3. die *Tornaria Chierchias* aus dem Pacific.

Grenachers Tornaria von den Cap Verden.
(*Tornaria Grenacheri* Spengel).

Von der durch Grenacher gesammelten Tornaria ist nach den obigen Ausführungen mit Sicherheit nur Folgendes bekannt. Sie ist eine tentaculate Form, ist als solche der *Tornaria Chierchiai* und *Tornaria Morgani* ähnlich. Ihre Höhe ist 5—9 mm, sie ist also die grösste bekannte Tornaria. Sie stammt von St. Vincente. Möglicherweise identisch mit *Tornaria Morgani* von den Bahamas.

Driesch und Herbst's Tornaria von Ceylon.
(*Tornaria* Sp. ?)

Ueber diese Tornaria ist nur bekannt, was Spengel in 3 Zeilen mitteilt (3, p. 379). „In allerjüngster Zeit habe ich 2 Larven, die ich *nach äusserlicher Untersuchung nicht von Tornaria Grenacheri unterscheiden kann*, durch die Güte der Herren Docs. H. Driesch und C. Herbst erhalten, die sie bei Ceylon gefangen haben". Daraus geht nur hervor, dass es sich um eine der *T. Grenacheri* jedenfalls sehr ähnliche tentaculate Form handelt. Weitere Angaben fehlen.

Chierchias Tornaria aus dem Pacific.
(*Tornaria Chierchiai*).

Unter 18° N., 175° W., zwischen den Sandwich- und den Marshall-Inseln.

Grösse: Höhe (Augenpol-After) 5 m.m.
Durchmesser $5^1/_2$ „

Äussere Merkmale: obere dorsale und ventrale Loben mit je 25—30 und mehr *secundären Loben* besetzt.

Dorsale Sättel breiter als ventrale.

Ventralsattel hoch und schmal.

Ventralband breit.

Lateralloben schmal mit 8 Tentakeln besetzt, untere Dorsalloben circa doppelt so tief wie die Lateralloben, ohne Tentakel.

Analfeld flach mit breitem primären circulären Wimperkranz und schmalen secundären Wimperkranz; Eichelporus tief liegend.

Scheitelplatte eine breite langgestreckte rechteckige Figur, die quer auf dem oberen Körperpol gelegen ist. Wimperschnüre verhalten sich in der Hauptsache wie bei *T. Mülleri* und *Krohnii*, mit dem Unterschiede, dass infolge der Breite der Scheitelplatte die Wimperschnüre längs die Ränder derselben eine Strecke weit ziemlich parallel mit einander verlaufen.

Augen liegen ganz nahe an einen der beiden Wimperschnüre (ventral oder dorsal?), haben complicierteren Bau als bei der Mittelmeerform.

Pigmentierung stark entwickelt. Dichte Reihe rotbrauner Flecken längs des oberen Randes des primären Wimperringes, zerstreute Pigmentflecken längs der Wimperschnüre, sehr grosse sternförmige Zellen unter dem Prae- und Postoralfeld.

Innere Organe: [in den Habitusbildern nicht eingezeichnet, aber aus guten Detaildarstellungen zu erkennen]. Dreiteiliger Darm, Oesophagus und Enddarm kurz. Mitteldarm ein cylindrisches Rohr, 6 mal so lang als breit, Wassersack im wesentlichen wie bei *T. Müllerii* und *Krohnii*. Sporne („zügelartige Fäden") symmetrisch entwickelt, eine grosse Strecke lang hohl.

Coelom. Kragencoelome [1]) liegen unmittelbar der Epidermis an als ein Paar sehr lang ausgezogener, daher in longitudinaler Richtung nur sehr schmaler Schläuche. Auf der ventralen Seite nur ein kurzes Stück von einander entfernt. „Von hier zog ein jeder in horizontaler Richtung in seinem Verlauf der postoralen Wimperschnur folgend rings um den Körper herum, bis auf die dorsale Fläche, um sich zuletzt etwas aufzurichten und, der linke in der Nähe des Eichelporus, der rechte in entsprechendem Abstande vom blinden Zipfel des „Wassersackes" zu endigen. Jeder entsandte ferner in der Gegend

---

1) Spengel sagt anfangs nicht, von welchen Coelomen die Rede ist. Erst aus den letzten Sätzen auf p. 432, sowie aus der Bemerkung auf p. 433: „Ganz anders verhalten sich die Rumpfcoelome", geht mit einiger Sicherheit hervor, dass er mit den fraglichen Bildungen die Kragencoelome gemeint hat. Ich halte sie jedoch auf Grund der Angaben Morgans und meiner Beobachtungen für die Rumpfcoelome. (S. o. S. 228/9). Die wirklichen Kragencoelome, die erst später angelegt werden, scheint Spengel nicht gesehen zu haben.

des Laterallobus einen langen dünnen Fortsatz nach oben. Wo er endigt, habe ich nicht beobachtet".

Die Rumpfcoelome liegen dem circumanalen Wimperring hart an. „Ueber ihre ventrale und dorsale Begrenzung habe ich keine Beobachtungen angestellt [1])."

Entwicklung: nur 1 Stadium bekannt, (etwa einer älteren Tornaria Krohnii entsprechend), alle weiteren Angaben unsicher.

Fundort: Pacifischer Ozean.

Bemerkung: Die *Tornaria Chierchiai* unterscheidet sich durch folgende Merkmale von der *Tornaria Morgani* (*Bahamas Tornaria*): sie besitzt etwas mehr, jedoch kürzere Tentakeln an den oberen Dorsalloben, unterer Dorsallobus ziemlich tief (*Morgani* hat keinen), der Mitteldarm ist viel länger, sie hat viel Pigment. Beide Formen haben jedoch die Grösse, das Coelom fern vom Darm, dem grossen Wimperring oder dem Ektoderm anliegend, gemeinsam, ferner den Bau der Scheitelplatte und der Augen.

Ritters Tornaria von Californien.
(*Tornaria ritteri Spengel*).

1. *Beschreibung im Zoolog. Anz.* Bd. 17, p. 24—30. Fig. 1.

Grösse (des conservierten Exemplars) Höhe: 1,9 mm.
Grösste Breite: 1,33 „

Äussere Merkmale: Obere dorsale Loben mit 2—4, obere ventrale Loben mit 6 Tentakeln besetzt. Tentakel kurz, dick, stummelförmig.

Ventralsattel: nicht hoch, breit.

Oralfeld sehr breit.

Unterer Dorsallobus?

Laterallobus ziemlich breit, analwärts, an der Mündungsstelle enge, mit 1 Paar Tentakeln besetzt.

Scheitelplatte wie bei der New England Tornaria Morgans (2, Taf. XXIV, fig. 7).

Augen weiter von einander entfernt als bei der *Bahamas Tornaria* Morgans.

Innere Organe: Weder aus der Beschreibung noch aus fig. 1 etwas bezüglich Magen und Coelome zu ersehen. Als Besonderheit wird nur erwähnt, dass die ersten Anlagen der Kiemenspalten nicht vor Eintritt der Metamorphose auftreten. Ferner wird ein Band

---

[1]) Was für Bildungen Spengel für „Rumpfcoelome" hält, ist schon wegen ihrer ganz ungewöhnlichen Lage am circumanalen (doch wohl dem secundären?) Wimperring ganz zweifelhaft. In Abb. 118 Taf. 25 allerdings sind sie dem Hauptwimperring (primären Wimperring) anliegend dargestellt!

hoher cylindrischer Epithelzellen am Grunde des Oesophagus genau beschrieben und funktionell als Endostyl gedeutet.

Entwicklung: nur 1 Stadium bekannt.

Fundort: Avalon, Island of Santa Catalina, Southern California.

2. *Beschreibung in University Calif. Publ. Zool.* Vol. 1. 1904, p. 171–203. Pl. XVII—XIX. insbes. fig. 1 u. 2.

Grösse (der lebenden Tornaria). Höhe: 2.07—2.32 mm.
Grösste Breite: 1.08—2.07 „

Äussere Merkmale: obere dorsale und ventrale Loben mit 6—8 Tentakeln, ferner 3 Tentakel auf dem schmalen Verbindungsstück (isthmus) zwischen beiden. Tentakel länger, abstehend.

Unterer Dorsallobus?

Laterallobus laut Abbildung ohne Tentakel [Laut Beschreibung mit 1 Paar Tentakel s. u.] Ventralsattel hoch.

Scheitelplatte? Augen?

Die Larve ist relativ breit im Verhältnis zu ihrer Höhe. Das Vorderende flach, die Analscheibe vorgewölbt. „The diameter of the body increases rapidly from the oral field backwards to the ciliary girdle so that the sides form an angle much less than a right angle with the plane of this circle." (5, p 174/5).

Secundärer Wimperkranz vorhanden.

Innere Organe: In fig. 2 auf Taf. XVII, ist der 3 teilige Darm eingezeichnet, an welchem der fast kugelige sehr grosse Magen auffällt.

Die weiteren Angaben betreffen das Ektoderm, das Blastocoel, das Magenepithel in verschiedenen Entwicklungsstadien u. kommen für die Charakterisierung dieser Tornarienform kaum in Betracht.

Entwicklung: nur 1 Stadium wird genauer beschrieben, von den älteren Stadien einige histologische Details angegeben.

Fundort: der gleiche, wie unter (1) angegeben.

Bemerkung: Beide Beschreibungen sind ungenau und stimmen in einigen Punkten nicht überein.

Ungenau sind sie, weil sie keinerlei Angaben über einige für die Charakterisierung der Tornarien wichtige Merkmale wie z. B. Dorsalloben, Coelom etc. enthalten. Wenn es auch denkbar ist, dass die Rumpf- und Kragencoelome in den geschilderten Stadien noch nicht ausgebildet waren — was ich jedoch nach den Erfahrungen bei den übrigen Tornarien für unwahrscheinlich halte — so ist doch bei so vorgeschrittenen Stadien mit so gut ausgebildeten Tentakeln das Eichelcoelom und die Herzblase etc. schon angelegt, doch fehlt auch hierüber jede Angabe.

Nicht übereinstimmen beide Beschreibungen:

1. in der Grösse.
2. in der Anzahl Beschaffenheit der Tentakel auf den Dorsalloben.
3. in der Form des Ventralsattels.
4. in der Beschaffenheit des Laterallobus.

Ich glaube hier nur auf den letzten Punkt eingehen zu müssen. In seiner 1. Mitteilung im Zool. Anz. bildet Ritter in Fig. 1 im Laterallobus ein Paar Tentakel bei *l'* ab. „In the narrow neck of this loop there appears to be the anlage of a single pair of processes like those found in the preoral portion of the band". Die weitere Bemerkung: „so far I am aware this loop does not exist in any other Tornaria" ist durch die späteren Untersuchungen der übrigen Tornarien überholt, wo sich regelmässig ein derartiger Laterallobus, mit oder ohne Tentakel, vorfindet.

In seiner 2. Mitteilung schreibt er p. 175: „A single pair of tentacles somewhat shorter than the longest ones of the series above described is present at the narrowest part of the lateral lobe". Dies stimmt nun wieder nicht mit seiner Fig. 2 u. 3 auf Taf. XVII. Wenn man diese Abbildungen betrachtet, ohne auf die Beschreibung Rücksicht zu nehmen, wird man wohl sagen müssen, dass die Lateralloben der dargestellten Tornaria tentakellos sind. Nun fasst Ritter aber hier offenbar die beiden Zipfel des ventralen Wimperbandes an der Mündungsstelle des Latterallobus als Tentakel auf, was er im ersteren Falle, bei der in Abb. 1. im Zool. Anz. dargestellten Form, augenscheinlich nicht tut. Halten wir auch in diesem Falle den gleichen Vorgang ein, so wäre hier der Laterallobus mit 2 Tentakelpaaren ausgestattet. Was ist also richtig?

Es ist wohl zweifellos, dass in beiden Fällen ein und dieselbe Tornarien-Form vorlag, da sie ja von demselben Autor an derselben Lokalität in verschiedenen Jahren beobachtet wurde. Doch ist dieselbe ungenau beschrieben.

Tornaria Sibogae Spengel.
(*Tornaria Spengeli*).

Grösse: *Höhe* 2,5—3 *mm.*

Grösste Breite im Wimperring 2 mm.

Äussere Merkmale: Dorsale und ventrale obere Loben mit circa 20 Tentakeln besetzt.

Hoher schmaler Ventralsattel.

Tiefer enger tentakelloser unterer Laterallobus.

(*Unterer*) *Dorsallobus tentakellos und etwa doppelt so tief wie der Laterallobus.*

Scheitelplatte quer verbreitert (?)

Augen in typischer Lage zwischen dorsaler und ventraler Area.

Analfeld: etwas vorgewölbt.

Innere Organe: *Darm*: Magen langgestreckt, erheblich seitlich zusammengedrückt. (Schrumpfung?)

Coelom: *Die Rumpfcoelome liegen nicht dem Epithel des Wimperrings an, sondern sind dem Darm sehr genähert, wo dicht über ihnen die Kragencoelome sich befinden.* Beide Paare sind schon so weit entwickelt, dass sie auf der dorsalen wie der ventralen Seite nicht mehr weit von einander entfernt sind. Das muskulöse Eichelcoelom geht nach hinten in einen rechten Blindsack aus, während sich der entsprechende linke Teil in die unpaare Eichelpforte mit dem Porus fortsetzt.

Entwicklung: nur eine Entwicklungsstufe bekannt (etwa einer älteren *Tornaria Krohnii* entsprechend).

Fundort: Siboga-Stationen 144, 165, 185, sämmtlich im Gebiet der *Molukken*, etwa zwischen Damar und Mysol.

Bemerkung: Das Material, welches Spengel vorlag, war in Formol conserviert und mangelhaft erhalten. Daher seine unsicheren Angaben über die Augen, Scheitelplatte, Darm, daher konnte den Abbildungen (9, p. 123, fig. S, T, U) nicht ein einzelnes Exemplar zugrunde gelegt werden, sondern dieselben sind „schematische Ansichten nach mittels Zeichenapparat entworfenen Skizzen".

Willeys Tornaria von New Britain.
(*Tornaria Willeyi*).

Grösse: ? [Ausser der Angabe, dass die Figuren bei 12 facher Vergrösserung gezeichnet sind, wird nichts darüber bemerkt].

Äussere Merkmale: Obere dorsale Loben mit circa 24, obere ventrale Loben mit circa 18 Tentakeln besetzt.

Ventralsattel sehr niedrig, flach.

Laterallobus breit mit circa 10 *Tentakeln besetzt, unterer Dorsallobus eine schmale tentakellose Rinne* (?).

Ventralband (spätere Kragenregion) sehr breit.

Circulärer grosser Wimperkranz verhältnismässig klein.

Scheitelplatte? Analfeld mässig vorgewölbt.

Augen liegen nicht in typischer Lage, sondern *innerhalb der ventralen Area.* (?)

Innere Organe: Darm sehr klein und schmal, Eichelcoelom sehr gross, muskulös, Eichelporus tief gelegen.

Coelome ?

Herzblase ∧ förmig.

Sporne ?

Entwicklung: nur 1 Stadium bekannt.

Fundort: Blanche Bay and off the small coral islands (Pigeon Island), New Britain.

Bemerkung: Von WILLEY's Tornaria liegt eigentlich keine Beschreibung vor, sondern die wesentlichen Merkmale — soweit dieselben von WILLEY festgestellt wurden — sind nur aus seiner sehr oberflächlichen Vergleichung mit der *Tornaria Grenacheri* SPENGELS und aus seinen 4 Abbildungen fig. 7, p. 286 zu erkennen.

„Among the external points of difference between my Tornaria and the *T. grenacheri* figured by SPENGEL may be mentioned those connected with the position of the eyes and the inferior dorsal lobe of the ciliated band. (Textfig. 4). In my Tornaria there is no such sharply defined lobe, but a groove passes continuously round from the lateral lobe of the ciliated band across the dorsal middle line. This groove is overhung by the anterior body of the Tornaria and appears in fresh surface view as a little more than a line. In MORGANS Tornaria the dorsal edge of the lateral lobe is entire there being no inferior dorsal lobe proceeding from it".

Das ist WILLEY's ganze „Beschreibung".

Der Verlauf der Wimperschnur wäre also ganz anders wie bei allen übrigen Tornarien, worauf SPENGEL bereits aufmerksam gemacht hat (9, p. 125). Während die Wimperschnur bei allen bekannten Tornarien continuirlich ist, wäre der Verlauf desselben bei der WILLEY'schen Tornaria unterbrochen. „Ich muss daher annehmen", schreibt SPENGEL (l. c.) „dass WILLEY's Beschreibung in diesem für die Charakterisierung einer Tornaria wichtigen Punkte ungenau ist." Ich stimme SPENGEL darin vollkommen bei und bin der Meinung, dass der abweichende Befund WILLEY's nur auf einen Beobachtungsfehler zurückzuführen ist.

Was die Augen betrifft, so schreibt WILLEY in der Figurenerklärung: „The eyes in (fig. D) are seen to lie within the limits of the ventral area bordered by the ciliated band. In other species they tend to lie centrally between the dorsal and ventral area." Dies stimmt allerdings für seine Figur D, betrachten wir jedoch seine Figuren A und B so sind in denselben die Augen ganz typisch am Apex eingezeichnet, je ein Auge zu beiden Seiten des das Eichelcoelom mit der Scheitelplatte verbindenden elastischen Stranges (*a m*) wie bei allen übrigen Tornarien. Ich muss daher WILLEY's Angaben betreffs der Augen gleichfalls für unsicher halten, ebenso seine Bemerkung betreffs des Pericards („note its ∧-shape").

In Willey's Beschreibung sind endlich Angaben über die Grösse und die Coelome nicht enthalten, sowie die 4 Figuren augenscheinlich in verschiedenen Maasstabe gezeichnet.

Im ganzen also eine sehr ungenaue Beschreibung, die sehr wesentliche Merkmale unberücksichtigt lässt und sicher unrichtige Angaben enthält.

Dennoch scheint hier eine von der *Tornaria Sibogae* Spengel's verschiedene Form vorzuliegen, da sie sich von ihr durch den sehr niedrigen Ventralsattel, die tiefe Lage des Eichelporus, und den mit 10 Tentakeln besetzten Laterallobus unterscheidet (Spengel). Ich füge noch bei, dass bei Tornaria Willeyi das Praeoralfeld viel breiter, der circuläre primäre Wimperkranz verhältnissmässig viel schwächer ausgebildet, das Analfeld und der Magen viel kleiner ist. Ferner liegt der Hydroporus bei Tornaria Willeyi links, bei *T. Sibogae* rechts von der Herzblase; die Herzblase ist bei *T. Sibogae* rundlich, bei Willey's Form hat sie die Gestalt eines /\.

Weldons Kleine Tornaria von Bimini Island (Bahamas Bank).

Morgans „*Bimini*" *Tornaria.* (*Tornaria Weldoni*).

Grösse: *Klein*, etwas mehr als halb so gross wie die „*Bahamas*" *Tornaria* Morgans (nach der Abbildung Taf. I. fig. 3).

Äussere Merkmale: *obere dorsale Loben mit* 5, *ventrale Loben mit* 6 *kurzen Tentakeln besetzt.*

Untere Dorsalloben?

Lateralloben breit, tentakellos.

Ventralsattel niedrig, ziemlich breit.

Ventralband nicht sehr breit.

Analfeld flach.

Secundärer Wimperring?

Scheitelplatte? *Verlauf der Wimperschnüre* nicht wie bei der grossen Bahamas Tornaria sondern *mehr wie bei der New England Tornaria*, indem dieselben in der Region der Augen nicht parallel laufen, sondern convergieren und dort verschwinden.

Innere Organe: 3 teiliger Darm.

Rumpf- und Kragencoelome dem Darm anliegend. Wassersack gut ausgebildet, mit der Apikalplatte durch einen contractilen Faden verbunden, durch den Eichelporus nach aussen mündend.

Entwicklung: Von dieser kleinen Tornaria sind ausser diesem, etwa

einer älteren *Tornaria Krohnii* entsprechendem Stadium MORGANS, noch ältere Stadien durch WELDON bekannt, die unmittelbar der Metamorphose vorangehen oder derselben bereits angehören. Ausser der geringen Grösse (0.8 mm. hoch, 0.4 mm. breit) zeigen diese älteren Stadien nichts characteristisches, für diese Form besonders eigentümliches.

Fundort: Bimini Island, Bahamas, [Aruba, Saba].

Bemerkung: Die obigen Angaben beruhen grössten Teils auf der schönen Abbildung MORGANS (4, Taf. I, fig. 12), denn er beschreibt die *Bimini Tornaria* nicht, sondern hebt nur ihre Unterschiede gegenüber die viel grösseren *Bahamas Tornaria* hervor. Im allgemeinen haben beide Formen denselben Habitus. Die *Tornaria Weldoni* ist jedoch viel kleiner, hat einen etwas anderen Verlauf des Wimperkranzes (?), geringere Anzahl von Tentakelchen, kürzere Tentakelchen, eine anders gebaute Apikalplatte, tentakellose Lateralloben und dem Darm anliegende Coelome.

Bezüglich des Verlaufes der Wimperschnur schreibt MORGAN (p. 25) folgendes: „The course followed by the anterior ciliated band differs from the Bahamas Tornaria in these respects: The lower horizontal limb of the anterior band does not turn forward at the middle of the side of the larva but continues toward the dorsal surface. Before reaching the mid-dorsal line it turns back again (on each side) to follow a parallel line as far as the middle of the side of the larva. Then it turns forward along the middle lateral area. The course of the band after this follows the path characteristic for Tornaria".

Ich bin mir nicht recht klar darüber geworden, was mit dieser Beschreibung gemeint ist. Ich glaube dieselbe so zu verstehen, dass MORGANS *Bimini-Tornaria* ziemlich lange untere Dorsalloben besitzen soll — was aus der Abbildung der in Seitenansicht dargestellten Larve nicht ersichtlich ist — die bei der Bahamas-Tornaria fehlen.

Gegenüber der Beschreibung MORGANS ergeben sich bei meinen *Tornarien Weldoni* von Saba und Aruba folgende Unterschiede:

1. Untere Dorsalloben sehr tief (vielleicht entfällt dies).
2. Ventralsattel hoch.
3. Analfeld vorgewölbt.
4. Secundärer circulärer Wimperring.
5. Bau der Scheitelplatte.

Trotz dieser Abweichungen beider Formen von einander halte ich dieselben doch für identisch.

Von der ebenfalls kleinen *Tornaria ritteri* unterscheidet sich die *Tornaria Weldoni* durch die ganz andere Körperform, die flache Analscheibe, den tentakellosen Laterallobus und das starke Pigment.

Weldons grosse Tornaria von Nassau, New Providence. Bahama Bank.
MORGANS *Bahamas Tornaria von North Bimini, Bahamas.*
(*Tornaria Morgani*).

Grösse: Höhe 4—4½ mm. [jüngstes Stadium 1¼ mm. hoch, etwas weniger breit].

Äussere Merkmale: obere dorsale und ventrale Loben mit circa 25 Tentakeln besetzt.

Ventralsattel nicht hoch.

Kein unterer dorsaler Lobus vorhanden. Laterallobus tief, mit ca 10 Tentakeln besetzt.

Analfeld eine ganz flache Scheibe. Secundärer Wimperkranz nur auf Schnitten nachweisbar.

Apicalplatte: „In the apical plate the anterior ciliated band breaks into four free ends, not united across from right to left and those on one side running parallel to one another".

Augen compliciert gebaut.

Pigmentflecke in der circumoralen Area im Schwinden (bei jüngeren Stadien stark ausgebildet).

Innere Organe: 3 teiliger Darm, relativ klein, Magen schmal.

Wassersack gross, mit Hydroporus, durch elastischen Strang mit Apicalplatte verbunden.

Coelome: Rumpf- und Kragencoelome nur auf Schnitten gesehen, stets entfernt vom Darm, in der Nähe des circulären Wimperkranzes oder des Ektoderms. Sporne gross.

Entwicklung: ältere Stadien der Metamorphose von WELDON, jüngere Stadien mit ca. 8 Tentakeln ohne Coelom bis einschliesslich der Metamorphose von MORGAN beobachtet.

Fundort: Bimini, Nassau, Bahamas, (Aruba, Saba) Die *Tornaria Morgani* von Aruba und Saba unterscheidet sich von der typischen *T. Morgani* durch folgende Merkmale:

1. durch die Grösse, (5—6 mm).
2. Tentakel etwas länger, etwas geringer an Zahl.
3. Ventralsattel hoch und schmal.
4. Analfeld nicht so hoch.

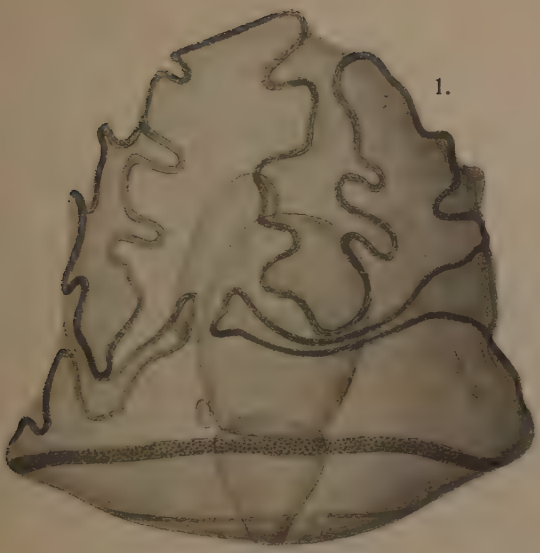
C. Geographische Verbreitung der tentaculaten Tornarien.

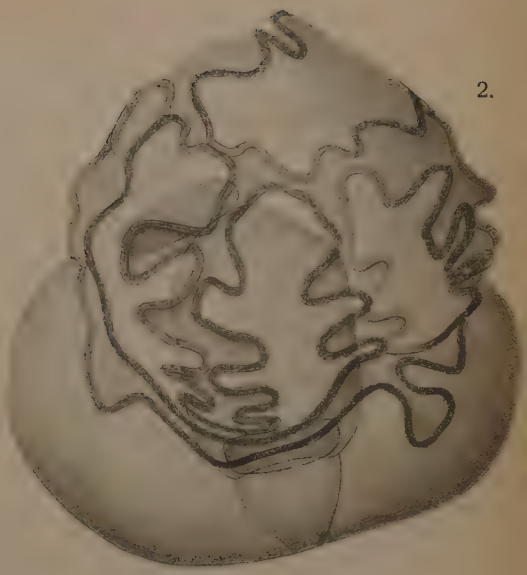
SPENGEL, der allerdings, mit einigem Zweifel, sämmtliche tentaculate Tornarien für einer einzigen Art angehörig betrachtet hat (3, p. 379), — ein Irrtum, den er später selbst zugegeben hat (im Sibogawerk 9, p. 124) —, schreibt ihnen circumterrane Verbreitung zu. Nachdem sich jedoch unter denselben eine ganze Anzahl wohl cha-

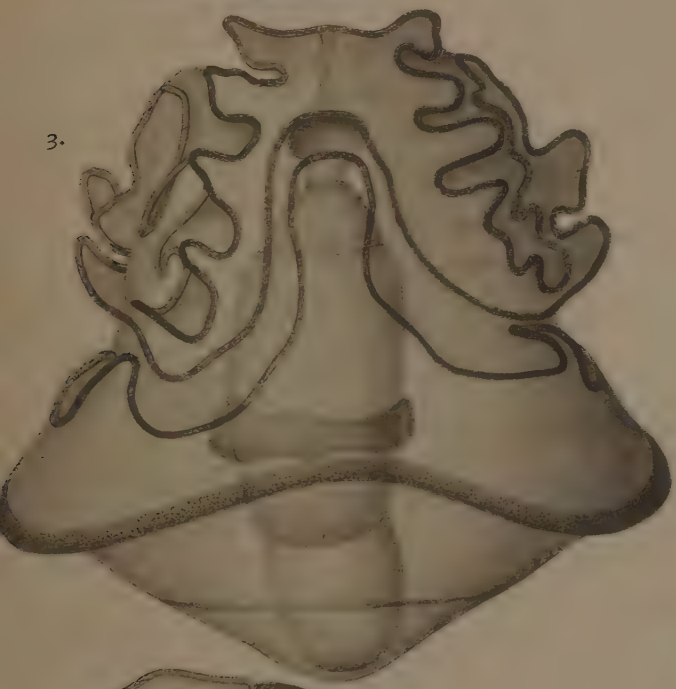
B. SYNOPSIS DER TENTACULATEN TORNARIEN.

	Höhe in mm.	Tentakel an Dorsal-loben	Untere Dorsalloben	Lateral Loben	Ventral Sattel	Analfeld	Scheitel platte	Augen	Pigment	Coelome	Sporne	Fundort
Tornaria Willeyi	?	18—24	Schmale Rinne? tentakellos	breit mit 10 Tentakeln	niedrig flach	mässig vorgewölbt	?	in ventraler Area	—	?	?	New Britain. Pacific
Tornaria Spengeli	3	20	tief tentakellos	tief tentakellos	hoch schmal	vorgewölbt	?	?	—	dem Darme anliegend	—	Molukken, Pacific
Tornaria Chierchiai	5	25—30	tief ohne Tentakel	mit 8 Tentakeln	hoch schmal	flach	breites Rechteck	compliciert	stark	fern vom Darm, am Wimperring oder Ektoderm	gross	Zwischen Sandwich und Marshall, Ins. Pacific
Tornaria Grenacheri	5—9	?	?	?	?	?	?	?	?	?	?	Cap verdische Inseln, Atlantic
Tornaria Weldoni *)	? klein	5—6	?	breit tentakellos	niedrig breit	flach	?	?	—	dem Darme anliegend	—	Bimini Island Bahamas, Atlantic
Tornari Morgani *)	4½	25	fehlen	tief mit 10 Tentakeln	nicht hoch	flach	breites Rechteck	compliciert	ge-schwun-den	fern vom Darm, am Wimperring oder Ektoderm	gross	Ebenda
Tornaria Ritteri 1.	1,9	4—6	?	1—2 Paar Tentakel?	?	?	wie bei der New England Tornaria	weit entfernt von einander	—	?	—	Avalon, Sta-Catalina Süd Californien, Pacific
Tornaria Ritteri 2.	2,32	6 - 8	?	1 Paar Tentakel	hoch	vorgewölbt	?	?	—	?	—	Ebenda
Tornaria sp.?	Nach äusserlicher Untersuchung von „*Tornaria grenacheri*" nicht unterscheidbar, von HERBST und DRIESCH bei Ceylon gefangen. (SPENGEL).											

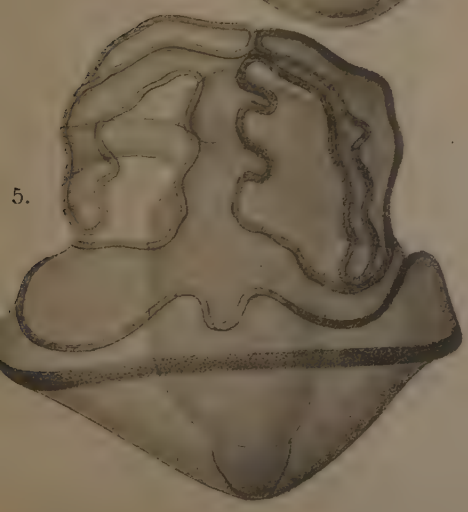
*) *Anmerkung.* Hier sind nur die Angaben in der Literatur aufgenommen. Die Unterschiede der mir vorliegenden von den typischen Tornarien sind oben auf S. 247 und S. 248 angegeben. Als Fundorte kommen noch Aruba und Saba hinzu.

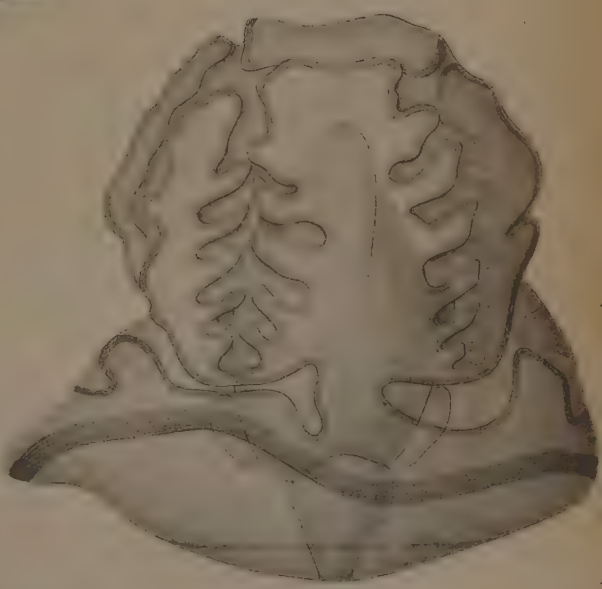

1.

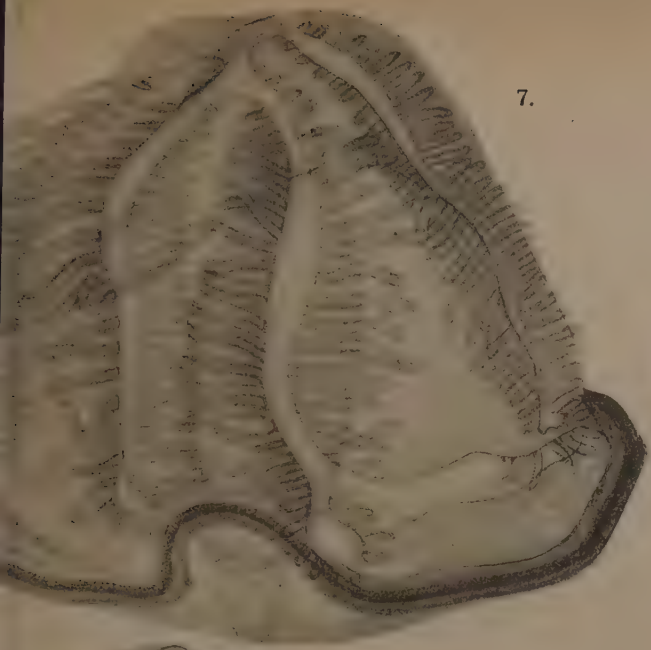

2.


3.

6.

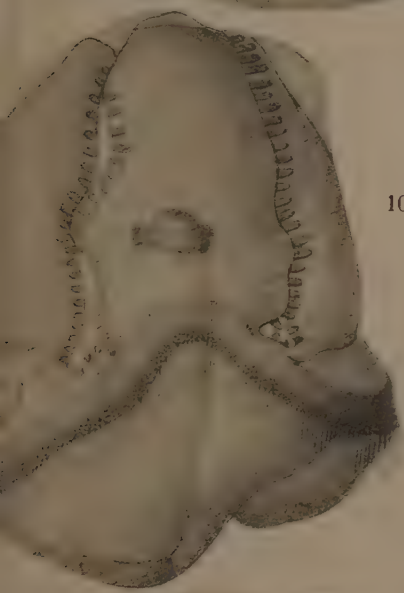

5.


4

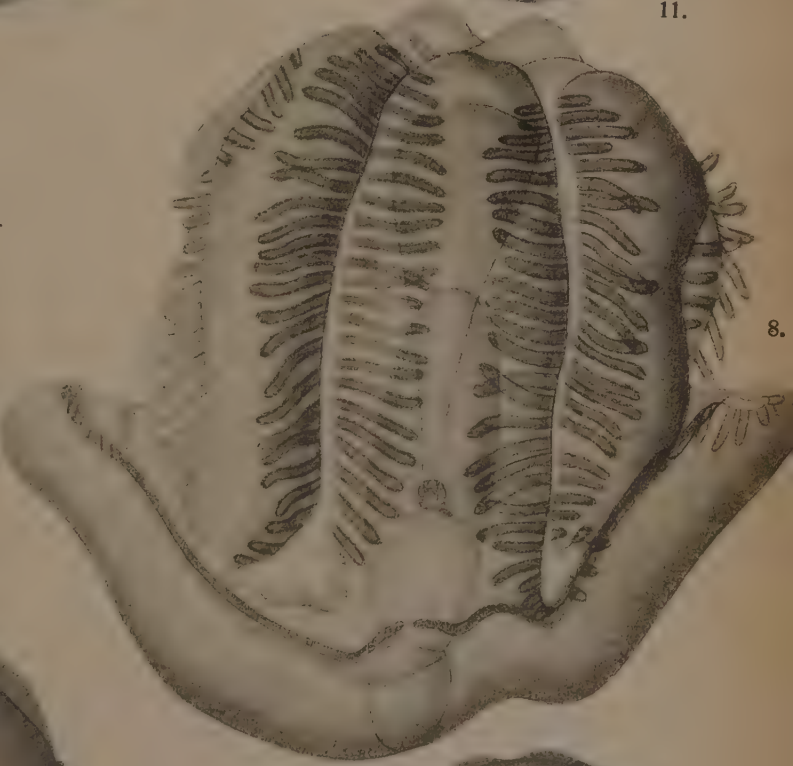


7.

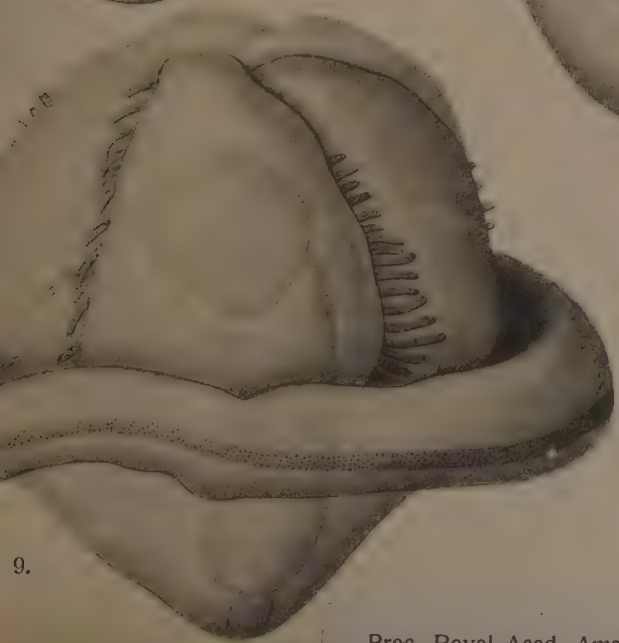
11.



10.



8.



9.

12.

rakterisierter Arten unterscheiden lässt, erweist sich diese Annahme als irrtümlich und mit der Unrichtigkeit der Praemissen sind natürlich auch die Schlussfolgerungen und Combinationen, die VANHÖFFEN an die angebliche circumterrane Verbreitung der einen Tornaria species geknüpft hat, gegenstandslos geworden. (7, p. 86, sowie Naturw. Wochenschr. Bd. XII, N°. 51, S 618). Nehmen wir die beiden tentakulaten Tornarien von der Westafrikanischen Küste und den Gewässern von Ceylon, über die wir ausser einigen Andeutungen SPENGELS fast gar nichts näheres wissen, als tatsächlich existierend an, so ergibt sich, dass *alle tentaculaten Tornarien nur in den warmen tropischen oder subtropischen Meeren vorkommen.* Nur aus dem romanischen Mittelmeer sind bisher keine tentaculaten Tornarien bekannt geworden. Auch in den kalten Meeren sind tentaculate Formen nicht nachgewiesen. Die tentaculaten Tornarien sind also echte Warmwasserformen, die im Litoral aller warmen Meere ihr Verbreitungsgebiet haben.

D. Verwandtschaft der tentaculaten Tornarien unter einander.

Von keiner einzigen tentaculaten Tornaria lässt sich zur Zeit mit Sicherheit angeben, zu welchem erwachsenen Tiere sie gehört. Da überdies die Mehrzahl der Tornarienspecies nur unvollkommen bekannt ist, kann man vorläufig über verwandtschaftliche Beziehungen derselben untereinander nur wenig sagen. Für die Beurteilung der Verwandschaft sind die Coelomverhältnisse von ausschlaggebender Bedeutung. In dieser Hinsicht können unter den tentaculaten Tornarien zwei Gruppen unterschieden werden: solche mit dem Darm anliegendem Coelom und solche bei denen dasselbe weit entfernt vom Darme peripher am Wimperring oder dem Ektoderm anliegend ausgebildet ist.

Zur ersteren Gruppe gehören *Tornaria Spengeli* und *Weldoni*, zur 2. Gruppe *T. Chierchiai* und *Morgani*. Die übrigen Formen lassen sich vorläufig noch nicht in diese Gruppen einteilen, da die Coelomverhältnisse bei ihnen nicht näher bekannt sind.

Die verschiedene Lage der Coelomsäckchen in beiden Fällen macht eine verschiedene Entstehungsweise derselben wahrscheinlich.

Bei *T. Spengeli* und *Weldoni*, welche die Coelomsäckchen in ganz gleicher Lage haben wie die *Tornaria Krohnii* des Mittelmeeres, dürften dieselben auch in gleicher Weise entstehen, nämlich durch Abschnürung von dem Darme.

Bei *T. Morgani* und *Chierchiai* ist dagegen die Entstehung der Coelomsäckchen aus Mesenchymzellen anzunehmen.

In der ersten Gruppe entstehen die Coelomsäckchen entodermal, bei der zweiten sind sie mesenchymatischen Ursprungs.

Tornaria *Morgani* und *Chierchiai*, welche auch in anderen Merkmalen mit einander übereinstimmen, sind jedenfalls nahe verwandte Formen.

Weiteres lässt sich vorläufig über die Verwandschaft der tentaculaten Tornarien untereinander nicht sagen.

Für die Ueberlassung der schönen, vortrefflich conservierten Planktonproben erlaube ich mir H. Prof. Dr. Max Weber meinen besten Dank zu sagen. Herrn Universitätszeichner Adolf Kasper, Wien, der die Abbildungen nach meinen Skizzen und Angaben an Hand des Originalmateriales ausführte, sage ich auch an dieser Stelle meinen besten Dank.

IV. *Replik auf einige Bemerkungen* Spengels.

Ich benütze diese Gelegenheit, um auf einige Bemerkungen Spengels, enthalten in seinem Referat (16, p. 55—57) über meine vorläufige Mitteilung (13), zurückzukommen.

Zunächst erklärt sich Spengel mit den von mir gebrauchten Bezeichnungen, „*Tornaria Mülleri*-Stadium" und „*Tornaria Krohnii*-Stadium" an Stelle seiner „*Tornaria Mülleri*" und „*Tornaria Krohnii*" nicht einverstanden, in dem sich seine Bezeichnungen auf „die voll entwickelten pelagischen Larven", nicht auf „Durchgangsstadien" beziehen. Ferner sei für *Tornaria Mülleri* die Tatsache charakteristisch, dass „ihr Wimperapparat auf dieser Stufe stehen bleibt und keine Secundär- und keine Lateralloben bildet, wie es bei Tornaria Krohnii geschieht, die eben in ihrem fertigen Stadium von der fertigen *T. Mülleri* verschieden ist".

Demgegenüber muss ich neuerdings erklären, dass ich meine Bezeichnungsweise aufrechthalte.

Die adriatische *Tornaria Mülleri* und *Krohnii* gehören in den Entwicklungskreis eines Tieres, des *Balanoglossus clavigerus*, was ich durch Züchtung nachgewiesen habe (14, 15). Nach Spengel gehört die Neapler *Tornaria Mülleri* und die *Tornaria Krohnii* nicht in den Entwicklungskreis desselben, sondern zweier verschiedener Enteropneusten. Nun habe ich aber durch Vergleich der Gradenser und Neapler Larven mit grosser Wahrscheinlichkeit feststellen können, dass sie identisch sind.

Die von Spengel behauptete geringere Entwicklung der Secundärloben bei der adriatischen Form kommt gegenüber der weit gehenden

Uebereinstimmung in anatomischer Hinsicht, (vergl. meine Ausführungen (15, p. 281/281)) wohl kaum als specifisches Unterscheidungsmerkmal in Betracht. Dass der Gradenser *Balanoglossus* eine von *clavigerus* verschiedene Art ist, wäre ja möglich, ist aber noch zu beweisen. Aus der Identität der adriatischen und Neapler Tornarien ergibt sich als logische Consequenz, dass auch die Neapler Formen zu einander gehören u. z. zu *Balanoglossus clavigerus*, der ja gleichfalls in der Umgebung Neapels nachgewiesen ist.

Ausser *Balanoglossus* (Ptychodera) *clavigerus* ist von Neapel und Umgebung nur *Ptychodera minuta Kow.* bekannt, die wahrscheinlich die von SPENGEL als *Tornaria dubia* beschriebene Larve hat. Es sprechen also alle Umstände für meine Auffassung.

Die übrigen Bemängelungen SPENGELS sind von geringerer Wichtigkeit.

Es ist richtig, dass die Bezeichnung des analen Teiles der Tornaria durch mich als „rückwärtig" zu beanstanden ist. Aber auch MORGAN spricht wiederholt in gleichem Sinne von „backwards" und es ist fraglich, ob die von SPENGEL gewählte Bezeichnung „unterer", „oberer" Teil passender und klarer ist. Jedenfalls dürfte doch jeder Leser wissen, welche Körperpartie gemeint war und das ist doch die Hauptsache.

Dass die erste Coelomanlage richtiger als „Kragen-Rumpfcoelom" zu bezeichnen wäre, da sich die Kragencoelome von derselben abschnüren, während ich die erste Coelomanlage als „Rumpfcoelom" bezeichnet habe, gebe ich ohne weiteres zu.

Leiden, Ende April 1920.

LITERATURVERZEICHNIS.

1. 1887. WELDON W. F. R., Preliminary note on a Balanoglossus-Larva from the Bahamas. Proceedings Roy. Soc. London. Vol. XLII.

2. 1891. MORGAN, T. H., The growth and development of Tornaria. Journal of Morphology, Boston, Vol. V.

3. 1893. SPENGEL, I. W., Die Enteropneusten des Golfes von Neapel, Fauna und Flora des Golfes v. Neapel. 18. Monographie, Berlin

4. 1894. MORGAN T. H, The development of Balanoglossus. Journ. of Morphol., Boston, Vol. IX.

5. 1894. RITTER WM. E., On a new Balanoglossus Larva from the coast of California and its possession of an endostyle. Zool. Anz. XVII. Jahrg. Leipzig.

6. 1899. WILLEY ARTHUR, Zoological Results. 16. Enteropneusta from the South Pacific, with notes on the west Indian species. Cambridge.

7. 1903. VANHÖFFEN ERNST, Die craspedoten Medusen der deutschen Tiefsee Expedition 1898—1899. I. Trachymedusen.

8. 1904. RITTER WM. E., and B. M. DAVIS, Studies on the ecology, morphology and speciology of the young of some enteropneusta of Western North America. Univ. Calif. Publ. Zool. Vol. 1.

9. 1907. Spengel I. W., Studien über die Enteropneusten der Siboga Expedition. 26. Monogr. Leiden.

10. 1911. Hensen Victor. Das Leben im Ozean nach Zählung seiner Bewohner. Ergeb. d. Planktonexp. Bd. V. O. Kiel, Leipzig.

11. 1911. Stiasny Gustav, Ueber adriatische Tornaria- und Actinotrocha-Larven. Sitz. Ber. Akad. Wien. 120. Bd. Wien.

12. 1913. Spengel I. W., Enteropneusta. In: Handwörterb. der Naturwissenschaften. 3. Bd. Jena.

13. 1913. Stiasny Gustav, Studien über die Entwicklung von Balanoglossus clavigerus D. Ch. (Vorläufige Mitteilung). Zool. Anz. 42. Bd. Leipzig.

14. 1914. ——, Studien über die Entwicklung der Balanoglossus clavigerus Delle Chiaje. I. Die Entwicklung der Tornaria. Zeitschr. f. wiss. Zool. 110. Bd. Leipzig.

15. 1914. ——, Studien über die Entwicklung des Balanoglossus clavigerus Delle Chiaje II. Darstellung der weiteren Entwicklung bis zur Metamorphose. Mitt. Zool. Stat. Neapel 22. Bd. N⁰. 8. Berlin.

16. 1915. Spengel I. W., Referat über die unter 13. erwähnte Arbeit. Zentralbl. f. Zoologie Bd. 5. Leipzig u. Berlin.

TAFELERKLÄRUNG.

Tafel I. stellt Entwicklungsstadien von *Tornaria Weldoni* dar.

Tafel II. stellt Entwicklungsstadien von *Tornaria Morgani* dar.

Die einzelnen Figuren werden im Texte erläutert.

Zoology. — *"Bemerkungen über einige Säugetierschädel von Sardinien."* By Dr. H. O. ANTONIUS. (Communicated by Prof. J. F. VAN BEMMELEN).

(Communicated at the meeting of June 26, 1920).

Das Zoologische Laboratorium der Universität Groningen bezog im Jahre 1911 durch einen Herrn GIRTANNER eine Serie von Säugetierschädeln aus Sardinien, die z. t. Haustieren, z. t. aber wilden Formen angehören. Die ersteren sollen in anderem Zusammenhang gewürdigt werden, über drei der letzteren aber möchte ich in folgendem einige Bemerkungen machen, weil sie mir besonderes Interesse zu verdienen scheinen.

Handelt es sich bei ihnen doch um jene merkwürdigen Formen, die durch ihre geringe, hinter jener der festländischen Verwandten weit zurückbleibende Grösse die Aufmerksamkeit seit langem auf sich gezogen und viel zu der Entstehung der Schlagworte, „Inselzwerg, Inselkümmerer" u. s. w. beigetragen haben. Zwei der Schädel gehören dem Rothirsche (Cervus elaphus corsicanus Erxl.), einer einem zwerghaften Individuum des europäischen Wildschweines (Sus scrofa L.) an. Ich gebe in den nebenstehenden Tabellen die wichtigsten Masse aller drei Schädel, neben jenen des Schweines — aus weiter unten ersichtlichen Gründen — auch noch die eines indischen Wildschweinschädels der Vittatus-Gruppe.

Für die *Hirsche* stand mir zur Zeit der Untersuchung kein Schädel eines erwachsenen festländischen Verwandten zur Verfügung, so dass ich auf direkte Massvergleichung verzichten muss. Immerhin fällt gegenüber dem Typus des mitteleuropäischen Rothirsches, wie er mir durch frühere Untersuchungen an rezentem und prähistorischem Materiale sehr geläufig ist, sofort die viel geringere Grösse auf, die jene eines starken Damhirsches nicht viel übertrifft, weiterhin aber auch gewisse Abweichungen in den Proportionen. Die Schädel sind nicht nur im ganzen kleiner, sondern namentlich im Facialteile viel kürzer, während die Breitendimensionen, insbesondere jene des Cranialteiles, von der allgemeinen Verkleinerung viel weniger betroffen erscheinen. Mit anderen Worten: sie entfernen sich in ihrem morphologischen Bild bedeutend weniger vom juvenilen Schädel, als solche der grossen europäischen Rothirschrassen oder gar solche der osteuropäisch-vorderasiatischen Marale: sie sind auf einem frühen Entwicklungsstadium stehen geblieben. Hievon abgesehen zeigen sie

keine besonderen morphologischen Verschiedenheiten. Caninen sind bei beiden Geschlechtern entwickelt, das Backenzahngebiss muss im Verhältnis zur geringen Gesamtgrösse sehr stark genannt werden, ist also von der allgemeinen Grössenreduktion nicht in gleichem Masse betroffen worden.

Der Schweineschädel gehört einem weiblichen Individuum an, das jedenfalls erwachsen gewesen ist, denn der letzte Molar steht nahezu voll in Usur. Die Gesamtform, insbesondere aber die schräge Stellung des Hinterhauptes ist die gleiche wie beim gewöhnlichen mitteleuropäischen Wildschwein, obwohl das Profil vor den Augen leicht konkav, die Stirnfläche über denselben aber in querer Richtung schwach konvex erscheint: offenbar auch eine Erinnerung an ein ontogenetisch früheres Entwicklungsstadium. Am interessantesten ist das Tränenbein, weil es ganz ausgesprochen den langen, niedrigen Typus des echten Sus scrofa zeigt und keinerlei Anklänge an die kürzere und höhere Form der Vittatus-Gruppe aufweist. Auch die verhältnismässig geringe Grösse und namentlich schmale Form des letzten Molaren ist ganz Scrofa-artig und verschieden von dem Typus des verglichenen Vittatus-Schädels. Die Backenzahnreihen liegen genau parallel, ohne also nach vorne zu divergieren, was ebenfalls einen gewissen Unterschied gegenüber Sus vittatus ergibt. Die Eckzähne sind infolge des weiblichen Geschlechtes klein, die für das männliche Geschlecht charakteristischen Unterschiede zwischen Sus scrofa und vittatus daher nicht zu konstatieren. Es erweist sich also dieser Schädel als solcher eines Wildschweines der Sus scrofa-Gruppe, ohne irgendwelche Anklänge an Sus vittatus. Dies ist deshalb interessant, weil auf Sardinien zwei dem Schädelbau nach verschiedene Wildschweintypen auftreten, eine gewöhnlich grössere von Scrofa-Habitus und eine kleinere mit engeren Beziehungen zu Sus vittatus. Der vorliegende Schädel beweist nun, dass auch die Scrofa-Rasse Sardiniens gelegentlich in ausgesprochenem Zwergwuchs auftritt. Das Vorkommen zweier verschiedener Wildschweine auf Sardinien glaubte noch C. Keller [1]) so auffassen zu müssen, dass nur die eine (Sus scrofa) ursprünglich wild, die andere dagegen aus entlaufenen Hausschweinen asiatischer Abstammung entstanden sei. Heute wissen wir durch die Untersuchungen S. Ulmanskys [2]), dass Wildschweine mit engeren Beziehungen zum indischen Sus vittatus viel weiter nach Westen verbreitet sind, als man früher angenommen hatte: mindestens bis Bosnien. Wahrscheinlich sind die nordafrikanischen Wildschweine,

[1]) Abstammung der ältesten Haustiere, Zürich 1902.

[2]) Mitteilungen d. landwirtsch. Lehrkanzeln a. d. K. K. Hochsch. f. Bodenkultur, Wien 1913.

über die bisher bedauerlich wenig Untersuchungen vorliegen, auch nichts anderes als derartige Uebergangsformen zwischen Sus scrofa und dem eigentlichen Sus vittatus, wie sie Ulmansky aus Bosnien nachgewiesen hat. Das Vorkommen zweier verschiedenen Typen auf dem immerhin kleinen Areal von Sardinien ist mit der Lage dieser Insel zwischen zwei Kontinenten leicht zu erklären: gelegentlich der ohne Zweifel wiederholt eingetretenen Landverbindungen konnten von Norden wie von Süden Formen einwandern. Zu ersteren gehören neben Sus scrofa vor allem der Rothirsch und der Muflon, zu letzteren neben dem Vittatus-ähnlichen Wildschweine die sardinische Wildkatze.

Die Untersuchung der vorstehend erwähnten zwerghaften Schädel war mir deshalb besonders interessant, weil sie mir Gelegenheit bot zu neuerlicher Beschäftigung mit der schon einmal von mir behandelten Frage der „insularen Zwergformen" unter den Säugetieren [1]). Es ist ja eine in der modernen Zoologie weit verbreitete Ansicht, dass grosse Säugetiere auf Inseln kleinere Lokalrassen bilden, als solche das benachbarte Festland bewohnen. Leider konnte ich nicht feststellen, wer diese Ansicht zuerst geäussert hat; am schärfsten ausgedrückt wurde sie wohl von H. Simroth, der in seiner „Pendulationstheorie" geradezu von einem „Gesetz der biologischen Abhängigkeit zwischen der Körpergrösse eines Tieres und des Areals, auf dem es lebt", spricht. Ich habe schon vor Jahren betont, dass es ein solches „Gesetz" m. E. nicht gibt, dass es vielmehr ein — allerdings menschlich durchaus begreiflicher — Beobachtungsfehler ist, wenn wir nach Prägung eines bestimmten Schlagwortes nur alle jene Fälle in unserem eigenen Bewusstsein registrieren, die ihm zu entsprechen scheinen, während die gegenteiligen uns gar nicht oder doch nur bei spezieller Beschäftigung mit der Frage zum Bewusstsein kommen. Ganz abgesehen von dem Verhalten der Reptilien und fluglosen Vögel, die bekanntlich gerade auf Inseln sehr grosse Formen erreicht haben, lassen sich auch unter den Säugetieren selbst so viele Fälle anführen, die dem fraglichen „Gesetz" widersprechen, dass dieses fast ebensoviele Ausnahmen aufweisen würde. Ich erinnere — um nur einige anzuführen! — an die mächtigen Esel von Malta und Pantelleria, ein richtiges Gegenstück zu dem Standardbeispiel der Shetlandponies, an den Riesenbären von Kadiak, die grösste Form der Braunbärengruppe, an den Canis antarcticus der Falklandsinseln, der seine festländischen Verwandten, die sogen. Azarafüchse, an Grösse weit übertrifft. Damit soll natürlich nicht das häufige Vorkommen von *Zwergformen auch auf Inseln* bestritten, sondern nur behauptet werden, dass sie ihre

[1]) Verhandl. Zool. Bot. Gesellsch. Wien, 1913.

Entstehung nicht einem mehr oder minder mystischen „Naturgesetz" verdanken, sondern genau den gleichen durchaus realen Umständen wie auf dem Festlande: eine Verschlechterung der Lebensbedingungen wird auf dem Festlande ebenso zu einem Rückgang in der Grössenentwicklung führen, wie auf einer Insel und dem Leben auf kleinen Inseln mag nur insoweit noch eine besondere Bedeutung für eine solche Grössenreduktion beizumessen sein, als es eine Abwanderung verhindert. Dieser Umstand kann eine Rolle gespielt haben bei der Entstehung der quartären Zwergelefanten in den Mittelmeerländern. Aber sogar in diesem Falle ist der Einfluss des Inselebens, so denkbar er an und für sich auch wäre, nicht ganz sicher. Denn gerade auf Malta kam auch, wie Knochenfunde beweisen, der riesige Elefas antiquus vor und das gegenseitige Altersverhältnis beider Typen auf der Insel scheint mir nicht über jeden Zweifel erhaben festgesetzt. Aber sei dem wie immer — für Hirsch und Wildschwein müssen wir jedenfalls andere Ursachen annehmen, die zu der auffälligen Grössenreduktion geführt haben. Ich glaube, dass diese bei beiden Formen nicht auf ganz gleiche, aber doch auf ähnliche Umstände zurückzuführen ist.

Was zunächst den sardinischen Rothirsch anbetrifft, so ist es eine auffällige Tatsache für jeden, der nicht nur rezentes, sondern auch subfossiles Material untersucht, dass die ganze europäische Gruppe der Edelhirsche sich seit der Pfahlbauzeit in auffallendem Grössenrückgang befindet. Edelhirsche, wie sie Ruetimeyer [1]) beschrieben hat, von der Grösse des Riesenhirsches oder eines starken Pferdes, sucht man heute auch in den besten ungarischen oder ostpreussischen Jagdrevieren vergebens, und in den ehemals kaiserlichen Gehegen in Niederösterreich erlegte noch Kaiser Josef II. (1780—1790) Hirsche, die die Grösse starker Wapitis erreicht, wenn nicht übertroffen haben, wie die erhaltenen Geweihe beweisen, während heute auch die stärksten Hirsche jener Gegenden weit hinter diesem Masse zurückbleiben. Je weiter nach Süden und Südwesten wir die Gruppe verfolgen, umso auffälliger wird dieser Rückgang: spanische und italienische Hirsche, die zur internationalen Jagdausstellung nach Wien gesandt wurden, also für ihre Heimat jedenfalls stark waren, nahmen sich neben dem Durchschnitt ihrer mitteleuropäischen Verwandten wahrhaft kläglich aus! Auch der festländisch nordafrikanische Hirsch (C. elaphus barbarus Benn.) steht an Grösse hinter diesen weit zurück, obwohl er immerhin noch grösser ist als der sardinische.

Dass dieser allgemeine Grössenrückgang der europäischen Rothirsche seine Ursache in einer Verschlechterung der Lebensbedingungen haben

[1]) Fauna der Pfahlbauten, Basel 1861.

muss, halte ich für sicher. Worin diese zu suchen ist, dafür gibt uns eben die auffallende Degeneration der südeuropäischen Hirsche einen Anhaltspunkt: es ist der Rückgang des europäischen Waldes in seiner ursprünglichen Form, der in Südeuropa fast ganz verschwunden, bezw. in Macchie verwandelt ist, während er in Mitteleuropa nur sehr vereinzelt seinen alten Habitus bewahrt, meist aber in den des Kulturforstes geändert hat. Dass sich viele, aber nicht alle Hirsche von Korsika und Sardinien durch sehr kurze, stämmige Beine auszeichnen, dürfte eine Folge des Lebens auf steilem felsigen Terrain sein; jedenfalls trägt auch diese Eigentümlichkeit viel dazu bei, die Tiere kleiner erscheinen zu lassen. Im Gewichte dürfte zwischen einem Durchschnittshirsch von Sardinien und einem normalen Berberhirsch kein nennenswerter Unterschied sein.

Aehnlich dürften die Ursachen gewesen sein, die zur Grössenreduktion der Schweine führten. Auch in diesem Falle haben wir einen allgemeinen Rückgang zu beobachten, aber er wird vielfach aufgehoben durch die Neigung der Wildschweine, einzelne Riesenindividuen hervorzubringen, ferner durch ihre ausserordentlich rasche Reaktion auf Veränderung der Futterverhältnisse — eine Reaktion, die sich naturgemäss ebenso gut in allgemeiner Grössenzunahme als auch im Gegenteile äussern kann. Es ist eine in Wildschwein-reichen Gegenden jedem erfahrenen Jäger bekannte Tatsache, dass einige aufeinander folgende Jahre mit besseren Eichel-oder Buchel-Ernten auch eine Zunahme der Wildschweine an Zahl und Grösse hervorrufen. Wenn wir also die Zwerghaftigkeit des sardinischen Wildschweines in der Hauptsache auf die gleiche Ursache zurückzuführen haben werden, wie jene der Rothirsche, so mag nebenher auch noch die rasche Degeneration, mit der gerade die Schweine auf nahe Inzucht reagieren, mitgewirkt haben. Andrerseits wird durch die oben angeführte rasche Grössenzunahme bei besseren Futterverhältnissen auch das gelegentliche Vorkommen einzelner grösserer Individuen erklärt, wie solche C. Keller erwähnt. Interessant wäre es, über die geographische Verbreitung beider auf der Insel festgestellten Schweinetypen etwas zu erfahren. Hierüber könnten aber nur sorgfältige systematische Aufsammlungen, wie sie bisher nicht vorliegen, Aufklärung bringen.

Zusammenfassend wiederhole ich, dass wir m. E. weder den Rothirsch noch das Wildschwein von Sardinien kurzerhand als „Inselkümmerer", „Inselzwerg", u.s.w. erklären können, dass vielmehr bei beiden die vorhandene Grössenreduktion auf andere, mit der Isolation gar nicht oder nur sehr indirekt zusammenhängende Ursachen zurückzuführen ist.

Herrn Prof. J. F. VAN BEMMELEN bin ich für die Erlaubnis zur Untersuchung der Schädel zu Dank verpflichtet.

TABELLE 1.

Hirsche: ♂ Nr. XXVI der Sammlung, von Villagrande, Ogliastra, Sard., 7. IX. 1909. M_3 fast in voler Usur, Incisivgebiss vollständig gewechselt, Gabelgeweih.
♀ Nr. XXV der Sammlung, von Arzana, Ogliastra, Sard., 11. VII. 1910. M_2 eben im Durchbruch, I_1 gewechselt.

	♂	♀
Scheitel länge (von der Mitte der Hinterhauptschuppe zum Vorderrand der Pmx)	308	276
Basilarlänge	274	246
Länge von der Mitte der Hinterhauptschuppe zum Hinterrand der Orbita	122	110
Länge vom Vorderrand der Orbita zum Vorderrand der Pmx	170	153
„ der Nasalnaht	95	83
„ vom Gaumenrand zum Vorderrand der Pmx	178	158
„ der Backenzahnreihe	101	—
„ vom vordersten Pm zum C	48	50
„ des Lacrymale (obere Naht)	50	48
„ der Orbita	45	41
Höhe „ „	43	40
Grösste Breite des Craniums	80	80
„ „ an den Orbiten	130	118
Breite an den Gehöröffnungen	88	80
„ „ „ Caninen	53	44
Höhe des Foramen magnum	24	25
Breite „ „ „	21	25
Höhe des „Rosenstocks" („pedicel")	28	—
Umfang der „Rose" („burr")	ca 120	—
Höhe der „Stange" („beam")	367, 365	—
„Auslage" (distance „tip to tip")	377	—

TABELLE 2.

Schweine: ♀, Nr. XLV der Sammlung, Gairo, Ogliastra, Sard., 12. VII. 08
♀, Nr. XLVII der Sammlung, annähernd gleichaltriger typischer Sus vittatus-Schädel aus Ostindien.

	Sard.	Ind.
Basilarlänge	235	268
Profillänge (Hinterhauptschuppe: Spitze der Nas.)	269	320
Länge vom Hinterrand des Gaumens zum Vorderrand des Pmx	162	196
Länge der Backenzahnreihe	90	110
„ vom vordersten Pm zum Vorderrand d. Pmx	69	91
„ „ Vorderrand der Orbita zum Vorderrand d. Pmx	172	208
„ der Nasalia (Naht)	127	158
Grösste Breite an den Jochbogen	114	136
Breite der Hinterhauptschuppe	54	66
Grösste Breite über den Orbiten	83	85
Geringste „ „ „ „	62	61
Breite am Hinterrand der Alveolen von M_3	39	39
„ „ Vorderrand „ „ „ P_1	33	38
Höhe vom Foramen magnum zur Hinterhauptschuppe	87	102
„ von der Spitze der Proc. jug. zur „	128	150
„ des Jochbogens	30	41
„ des Tränenbeins	20	26
Länge „ „ an der oberen Naht	48	46
„ „ „ „ „ unteren „	24	25
Höhe des Foramen magnum	25	21
Breite „ „ „	19	22
Länge des Unterkiefers vom Gelenk zur Spitze der Inc.-Alveole	209	237
Höhe des Unterkiefers vom Gelenk zur Tischplatte	86	103
Grösste Breite des Unterkiefers in der gegend des M_2	71	88
Länge der Backenzahnreihe	86	114
„ des M_3 im Oberkiefer	24	30
„ „ „ „ Unterkiefer	26	38
Breite „ „ „ Oberkiefer	15	21
„ „ „ „ Unterkiefer	13	18

Zoolog. Laboratorium der Universität.
Groningen, Ende Juni 1920.

Chemistry. — "*Catalysis* — Part VII — *Temperature Coefficient of Physiological processes*". By Dr. NIL RATAN DHAR. (Communicated by Prof. ERNST COHEN).

(Communicated at the meeting of May 29, 1920).

In this article it is proposed to subject to critical examination the results obtained with regard to the effect of temperature on physiological processes. Before proceeding to the consideration of these reactions I shall briefly state the results obtained in the case of purely chemical reactions and then try to show how far these relations are applicable to physiological changes.

In homogeneous medium the following general results have been obtained.

a. The higher the order of the reaction, the smaller is the coefficient of temperature, in other words, unimolecular reactions have higher temperature coefficients than polymolecular reactions under identical conditions.

b. The greater the velocity of a reaction the smaller is the temperature coefficient.

c. The temperature coefficient of a positively catalysed reaction is smaller than that of the uncatalysed reaction and the greater the concentration of the catalyst the greater is the fall in the temperature coefficient.

In the case of negative catalysis, a reaction which is catalysed (negatively), has a higher temperature coefficient than the uncatalysed reaction. In this case, the greater the concentration of the catalyst the greater is the increase in the temperature coefficient.

In the case of heterogeneous reactions, the following points have been established :

a. Diffusion is the guiding factor in the velocity of heterogeneous reactions.

b. With heterogeneous catalysts which cause reaction between the substance in question to take place with practically infinite velocity, the actual rate of reaction will be determined solely with which the substance is diffused to the surface of the catalyst.

c. If the heterogeneous velocity is that of the diffusion process, one will always get a unimolecular coefficient for the reaction in question, independent of the actual order of the more rapid chem-

ical reaction, which accompanies the diffusion process. Hence it is useless to try and determine the order of a heterogeneous reaction, from the velocity with which it proceeds.

d. The temperature coefficients of heterogeneous reactions are small, (viz, about 1.2 for a 10° rise).

In this connection it is interesting to note that photo-chemical reactions have small temperature coefficients (viz. about 1.1 for a 10° rise).

Now I shall discuss the results obtained in physiological processes with regard to the influence of temperature on them.

The relation between the temperature and the velocity of respiration has been studied during the last few years both for plants and animals. The principal object of these investigations has been to find out whether respiration can be considered as a chemical process.

From the researches of CLAUSEN (Landwirt. Jahrbuch Bd. **19** 1890), BLACKMAN (Annals of Botany 1905, **19**, 288), KUIJPER (Rec. Trav. Bot. Néerl. 1910, **7**, 131) LEHENBAUER (Physilogical researches N°. 5, AUGUST 1914), Miss LEITSCH (Annals of Botany January 1916), Miss SAUNDERS (private communication) and others we find that the temperature coefficients of plant processes generally lie between 2 and 3 for a 10° rise of temperature.

BROWN and WORLEY (Proc. Roy. Soc. 1912, **85** B, 546) have shown that the temperature coefficient of the velocity of absorption of water by different seeds is about 2 for a 10° rise. If the values of the velocity coefficients are calculated from their results, we see that they follow the unimolecular formula.

The researches of VELEY and WALLER (Proc. Roy. Soc. 1910, **82** B) show that the ARRHENIUS formula can be applied to the influence of temperature on the velocity of the action of drugs on muscles.

Very large number of experiments have been made on the influence of temperature upon metabolism both in cold-blooded and in warm-blooded animals. But comparatively few of them have been made under standard conditions. In most cases animals have been free to move about and even in cases where they have been tied, muscular movements have not been prevented or muscular tone abolished. In these conditions a fundamental difference has been observed between the effects of temperature upon cold-blooded and upon warm-blooded animals. In cold blooded-animals the respiratory exchange almost always rises with increasing temperature, but generally irregularly and to a very different degree in different animals.

In the case of bees Marie Parhon (Ann. des Sc. nat. Zoo. Sér., 9, **9,** 1—58) finds that the temperature in the cluster of bees inside the hives shows a very striking constancy throughout the year.

In intact warm-blooded animals, a fall in the surrounding temperature regularly causes an increase in the respiratory exchange thanks to the mechanism of "Chemical heat regulation".

In all the experiments so far mentioned both on cold-blooded and on warm-blooded animals we have to do with two distinct effects of temperatnre, viz. one upon the central nervous system causing variation in the innervation of different organs and especially of the muscles and one upon the tissues themselves influencing the reaction velocity of the metabolic processes.

In the warm-blooded animals the action of low temperature on the skin produces reflexly innervation of the muscles resulting either in movements or in increase of tone.

In the cold-blooded animals the processes in the central nervous system itself are probably acted upon, and increased muscular activity is produced by increasing temperature except in the cluster of bees which in the aggregate reacts against the temperature somewhat after the fashion of a warm-blooded animal.

When the influence of temperature on the metabolic process is to be studied, the nervous influence must be excluded, and the experiments must be made under standard conditions.

It has been found repeatedly both on man and on animals that even a slight increase in body temperature over the normal produces an increase in the standard metabolism.

It follows from the experiments of Krogh (Biochem. Zeit. **1914, 62,** 266) and others that the velocity of catabolic reactions increases in all animals with rising temperature up to a maximum at and above which temperature has deleterious effect upon the organism. The maximum temperature probably differs considerably for different animals, but very few determinations have been made so far.

The more rigorously standard conditions are maintaind, the more regular is the influence of temperature observed.

Chick and Martin (Journal of Physiol. **45,** 40) find that the coagulation of haemoglobin by heat has the temperature coefficient 13.8 for the elevation of 10°, whilst in the case of albumen it is higher. In this connection it is interesting to note that Von Schroeder (Zeit. Phys. Chem. 1903, **45**, 75) has found that a solution of gelatine has a viscosity of 13.76 at 21° C. and 1.42 at 31° C. i. e. about 10 times less with an elevation of 10°.

The results obtained by Chick and Martin show that the temper-

ature coefficient of coagulation of proteins by water is an exceedingly high one compared with effect of temperature on most chemical reactions. In the majority of instances the reaction velocity is increased about 1.1 times for 1° C. i. e. 2 to 3 times for a rise of temperature of 10°. Even the biological processes of germination of seeds, respiration of plants and growth of bacteria fall within this range.

On the other hand many reactions in which complex protein bodies are concerned have been shown to possess high temperature coefficients which are comparable with those obtained for heat coagulation. The destruction of emulsin by heat has according to Tammann (Zeit. Phys. Chem. 1895) a temperature coefficient of about 7.14 for a 10° rise between 60° and 70°. Bayliss (1908) found the action of trypsin to be hastened 5—3 times for some germs in accordance with a logarithmic law. Ballnev (1902) found the disinfection of anthrax spores by steam to take place from 9 to 11 times more quickly by raising the temperature 10° and the law of Arrhenius is equally applicable to his results.

Chick and Martin (loc. cit) have shown that the disinfection of vegetative forms of bacteria with phenol and other coal-tar derivatives has a temperature coefficient of 8 to 10 for a 10° rise of temperature.

On the other hand the disinfection by Silver Nitrate and Mercuric Chloride has a much lower coefficient and that is about 2.

The high temperature coefficient for the coagulation of egg albumen has a counterpart in that for the velocity of destruction by hot water of the haemolysins in vibriolysins, tetanolysin and goat serum.

Madsen and his collaborators found the influence of temperature to be in accordance with the law of Arrhenius and the velocity of this reaction to be doubled if the temperature were raised 1° C. They also showed that the action of hot water upon some agglutinins to be similarly influenced by temperature.

This marked influence of temperature is extremely useful for men and animals. When a toxin enters the system, the temperature of the body rises by two or three degrees and we get the phenomenon of fever and the poison is destroyed about 10 or 20 times more quickly at this fever temperature.

Hartridge (Jour. of Physiol. 1912, Vol. XLIV, 34) finds the temperature coefficient for heat coagulation to be as great as 726 for a 10° rise for some protein matter. In this connection it is interesting to note that the decomposition of sulphur trioxide by heat has 419 for its temperature coefficient for a 10° rise at about 30°.

Watson (Jour. Hygiene 1908, **8**, 536) applying Ostwald's isolation method to Miss Chick's results finds that in the disinfection of certain

bacteria with phenol, the molecules (N) of phenol reacting with those of the bacterial constituent are in the proportion of 5.5 to 1. As regards the metallic salts the same law holds good for disinfection by silver nitrate and the molecules (N) of silver nitrate reacting with those of bacterial constituents are in the proportion of 1 : 1. In the case of Mercuric chloride, however, the above relation between the concentration of disinfectant and the average velocity of disinfection is maintained only if the former is expressed in terms of the corresponding concentration of mercuric ions. Under these circumstances, N has the value 4.9 for anthrax spores and 3.8 for paratyphosus. But the temperature coefficient of the disinfection by phenol is very high, though the reaction is approximately heptamolecular. On the other hand, in the case of silver nitrate the reaction is approximately bimolecular and the temperature coefficient is small viz. 2 for a 10° rise. These results are contrary to our experience in ordinary chemical reactions, where the greater the order of a reaction the smaller is the coefficient of temperature.

Kanitz (Temperature und Lebensvorgänge,, 1915), Snyder (Amer. Jour. of Physiol. **22**, 1908, 309), Cohen Stuart (Proc. K. Akad. Wetensch. Amsterdam, 1912, **20**, 1270), Pütter (Zeit. Allg. Physiol 1914, **16**, 617) and others have tried to represent the influence of temperature on physiological processes by the rule of van 't Hoff, but it is not very important whether the temperature coefficient has the value 2 or 3, the important point to establish is whether the formula of Arrhenius (Zeit. Phys. Chem. 1889, **4**, 226) or the formula of Harcourt and Esson (Phil. Trans series A Vol. **186**, 817 (1895), Vol. **212**, 187, (1912), which is applicable to ordinary chemical reactions, is also applicable to physiological processes.

Blackman (Annals of Botany 1905, **19**, 281) has accepted the validity of the van 't Hoff rule and has found the value 2.1 between 9° and 19°. He has assumed that this value of the temperature coefficient remains constant at higher temperatures; this assumption is contrary to our experience in ordinary chemical reactions, the temperature coefficient for a 10° rise becomes smaller as the temperature rises. This falling off of the temperature coefficient with increase of temperature is also expected from the Arrhenius formula. Evidently the conclusions of Blackman would have been more correct had he accepted the Arrhenius formula.

Looking at the whole problem from a broad point of view it seems that temperature has two effects on vital processes: — (a) the increase of the velocity of the chemical reaction involved in the physiological changes, (b) the destruction of the living cells.

At low temperatures the first effect is predominant since the harmful effect does not begin to play its part.

Thus the problem for us is to investigate the effect of temperature on vital processes at low temperatures that is, before the harmful effect on the living cells has begun and we shall probably see the same quantitative laws which are applicable in the domain of ordinary chemical reactions *in vitro* are also applicable to vital processes taking place in nature.

Enzymes and colloids reign supreme in life processes and the BROWNIAN movement of these particles does away with the diffusion layer characteristic of heterogeneous reactions and makes them analogous to positively catalysed reactions taking place in homogeneous medium and hence we expect to find the same laws governing both ordinary chemical reactions and life processes, compare DHAR, Proc. Akad. Wetensch. (1919).

In conclusion I suggest that it is desirable to study the problem of acclimatization scientifically from the point of view of the influence of temperature on life processes.

SUMMARY.

a. Physiological processes take place mostly in heterogeneous medium. The Brownian movement of the colloidal particles present in the reacting substances does away with the diffusion layer characteristic of heterogeneous reactions and makes the physiological reactions similar to positively catalysed reactions taking place in homogeneous medium. Consequently the temperature coefficients of physiological processes instead of being small (Viz. about 1.2) are generally greater than 2 for a 10° rise.

b. The spontaneous destruction of certain toxins is highly influenced by temperature and this fact is extremely useful to the human body because in the phenomenon of fever the poison is killed very rapidly.

c. Before the destructive effect of temperature begins to set in, the ARRHENIUS formula connecting temperature and velocity is generally applicable to physiological processes.

Chemical Laboratory, Muir Central college,
Allahabad (India).

Chemistry. — *"Sur une classe de fonctions admettant une dérivée seconde généralisée"*. By Prof. ARNAUD DENJOY.

(Communicated at the meeting at May 29, 1920).

Considérons une série trigonométrique partout convergente

$$f(\theta) = a_0 + A_1 + A_2 + \ldots + A_n + \ldots, \quad . \quad . \quad . \quad (1)$$

où $A_n = a_n \cos n\theta + b_n \sin n\theta$; a_0, a_n, b_n étant indépendants de θ. Soit $B_n = -b_n \cos n\theta + a_n \sin n\theta$. Intégrons terme à terme la série (1), et posons:

$$\varphi(\theta) = a_0\theta + C + B_1 + \ldots + \frac{B_n}{n} + \ldots \quad . \quad . \quad . \quad (2)$$

en tout point θ où la série du second membre converge. Aux points où cette série diverge, nous dirons que $\varphi(\theta)$ n'existe pas. C est quelconque, indépendant de θ. Intégrant une fois de plus, nous trouvons:

$$F(\theta) = \frac{a_0}{2}\theta^2 + C\theta + C' - A_1 - \ldots - \frac{A_n}{n^2} \ldots \quad . \quad . \quad (3)$$

C' étant, comme C, indépendant de θ.

RIEMANN a montré que la fonction continue $F(\theta)$ admet $f(\theta)$ pour dérivée seconde généralisée, c'est-à-dire que, si

$$R(\theta, u) = \frac{F(\theta + u) + F(\theta - u) - 2F(\theta)}{u^2},$$

on a $f(\theta) = \lim_{u=0} R(\theta, u)$, quel que soit θ indépendant de u.

Nous nous proposons dans cette note d'étudier les propriétés différentielles du premier ordre de la fonction $F(\theta)$. Il est bien connu que, si $F(\theta)$ possède au point θ_0 une dérivée $F'(\theta_0)$, la série (2) converge au même point et l'on a $\varphi(\theta_0) = F'(\theta_0)$. La réciproque est exacte. Donc, $\varphi(\theta)$ et la dérivée de F existent ou non simultanément, et coïncident chaque fois qu'elles existent.

Posons

$$Q(\theta, u) = \frac{F(\theta + u) - F(\theta)}{u}$$

On montre que:

$$Q[\theta, u] - \left(a_0\theta + C + B_1 \ldots + \frac{B_n}{n}\right)$$

tend vers 0 avec u, si $n|u|$ reste compris entre deux nombres

positifs indépendants de u. Les propriétés différentielles du premier ordre de $F(\theta)$ et le mode de convergence ou de divergence de la série (2) sont ainsi étroitement liés.

n étant choisi comme il vient d'être dit, la différence

$$Q[\theta + \mu u, \lambda u] - \left(a_0 \theta + C + B_1 + \ldots + \frac{B_n}{n}\right)$$

tend aussi vers 0 avec u, *uniformément* dans le champ : θ quelconque, μ, λ, $\frac{1}{\lambda}$ bornés. Enfin, si $p_0 + p_1 + \ldots + p_r = 0$, l'expression

$$p_0 Q[\theta, u] + p_1 Q[\theta + \mu_1 u, \lambda_1 u] + \ldots + p_r Q[\theta + \mu_r u, \lambda_r u]$$

tend *uniformément* vers 0 avec u dans le champ : θ quelconque,

$$\sum_0^r |\mu_i + 2\lambda_i||p_i|\ ,\ \sum_0^r \mu_i^2 |p_i|\ ,\ \sum_0^r \lambda_i^2 |p_i|\ ,\ \sum_0^r \left|\frac{p_i}{\lambda_i}\right|$$

tous bornés ($\mu_0 = 0, \lambda_0 = 1$).

La démonstration se fait en remarquant que, si $\sqrt{a_n^2 + b_n^2} = \varrho_n$, ϱ_n tend vers 0, d'après la convergence de la série (1). Donc, si

$$\sum_1^n \varrho(m) = n\,\omega(n)\ ,\ \sum_1^n m\,\varrho(m) = n^2\,\omega'(n)\ ,\ \sum_{n+1}^{\infty} \frac{\varrho(m)}{m^2} = \frac{\omega''(n)}{n},$$

les coefficients $\omega(n)$, $\omega'(n)$, $\omega''(n)$ tendent vers 0 quand n croît.

On a :

$$A_m(\theta + u) = A_m(\theta)\cos mu + B_m(\theta)\sin mu.$$

D'où

$$A_m[\theta + (\lambda + \mu)u] - A_m[\theta + \mu u] = A_m(\theta)[\cos m\overline{\mu + \lambda}\,u - \cos m\mu u] + \\ + B_m(\theta)[\sin m(\mu + \lambda)u - \sin m\mu u].$$

Si $m \leqq n$, nous transformons les coefficients de $A_m(\theta)$ et $B_m(\theta)$ par les formules :

$$\cos\beta - \cos\alpha = \delta\frac{(\beta^2 - \alpha^2)}{2}\ (\delta^2 < 1)$$

$$\sin\beta - \sin\alpha = (\beta - \alpha)\left[1 - \theta\frac{\beta^2 + \alpha\beta + \alpha^2}{6}\right]\ (0 < \theta < 1).$$

Si $m > n$, nous remplaçons les mêmes coefficients par 2δ, $2\delta'$ avec δ^2, $\delta'^2 < 1$.

Les résultats énoncés paraissent alors en évidence. Sous leur forme la plus simple ($p_0 = -p_1 = 1, p_1 = 0, p_2 = \ldots = 0$), la propriété que $Q[\theta, u] - Q[\theta, \lambda u]$ tend *uniformément* vers 0 avec u, dans le champ : θ quelconque, λ et $\frac{1}{\lambda}$ bornés, donne lieu à la remarque suivante.

Soit d un *nombre dérivé* (extrême ou médian) [1]) de F au point θ. Il existe alors une suite de nombres de même signe $h_1, h_2, \ldots, h_n, \ldots$, tendant vers 0 et tels que: $\lim_{n\,\infty} Q[\theta, h_n] = d$. Soit α un nombre superieur à 1, aussi grand que nous le voudrons, indépendant de n. Considérons l'ensemble E formé des intervalles i_n et i'_n ainsi définis: i_n est l'intervalle $\theta + \frac{|h_n|}{\alpha}$ à $\theta + \alpha|h_n|$; i'_n est l'intervalle $\theta - \alpha|h_n|$ à $\theta - \frac{|h_n|}{\alpha}$. θ est évidemment un point limite de E. Or, quelle que soit la façon dont un point $t = \theta + h$ tende vers θ sans quitter E, $Q[\theta, h]$ tend vers d.

Nous disons alors que $F(\theta)$ admet au point θ une *dérivée spéciale* à E, égale à d.

La propriété étant exacte quel que soit α invariable, il est possible de choisir α croissant indéfiniment avec n, assez lentement pour que la propriété subsiste sur l'ensemble Ea ainsi obtenu. Donc,

Si d est un nombre dérivé extrême ou médian de $F(\theta)$, d est la dérivée de $F(\theta)$ spéciale à un ensemble Ea dont l'épaisseur supérieure au point θ est 1 bilatéralement [2]).

Supposons que le *rapport* $\frac{h_n}{h_{n+1}}$ *soit borné indépendamment de n* (mais non de θ). Alors, si $1 < \left|\frac{h_{n+1}}{h_n}\right| < l$, choisissons $\alpha > \sqrt{l}$, et

---

[1]) On appelle *nombre dérivé* de F l'une quelconque des valeurs limites d de $\frac{F(\theta+u)-F(\theta)}{u} = Q(\theta, u)$ quand u tend vers 0 avec un signe invariable, θ demeurant fixe. d est un nombre dérivé *droit* si $u > 0$, *gauche* si $u < 0$. d est un *dérivé extrême*, soit *supérieur*, soit *inférieur*, si d est l'une des limites extrêmes, soit la plus grande, soit la plus petite, de $Q(\theta, u)$ quand u tend vers 0, avec un signe déterminé.

Tout nombre compris entre les dérivés extrêmes de F pour un côté donné, est appelé nombre *dérivé médian* pour le même côté.

[2]) Soit $m(x)$ la mesure de la partie d'un ensemble donné E comprise entre un point fixe a et un point quelconque x. $m(x)$ a le signe de $x - a$, à moins d'être nul. On appelle *épaisseur supérieure droite*, *épaisseur inférieure droite*, *epaisseur supérieure gauche*, *épaisseur inférieure gauche* de E en un point x_0, les nombres dérivés de même qualification respective de la fonction $m(x)$ en x_0. Ces nombres dérivés appartiennent au segment (0,1), (c'est à dire à l'ensemble des nombres μ tels que $0 \leq \mu \leq 1$). On dit que E possède en x_0 une épaisseur (sous-entendu bilatérale) ou une épaisseur droite, ou une épaisseur gauche égales à λ en x_0, si $m(x)$ admet en x_0 le nombre λ respectivement pour dérivée (ordinaire, bilatérale) ou pour derivée droite ou pour dérivée gauche. On sait que les points de E où E n'a pas l'épaisseur 1 forment un ensemble de mesure nulle (Lebesgue).

construisons comme il a été dit plus haut les intervalles i_n, i'_n. Quelque soit n, i_n et i_{n+1} ont une partie commune, et il en est de même de i'_n et de i'_{n+1}. L'ensemble E formé des i_n et des i'_n contient tout l'intervalle $\theta - \alpha |h_1|$ à $\theta + \alpha |h_1|$, sauf le point θ. Donc $F(\theta)$ *admet d pour dérivée* (ordinaire, ou générale) *au point* θ.

En nous plaçant à un autre point de vue, il nous sera possible d'étendre et de préciser les propriétés connues de l'ensemble E où existe $\varphi(\theta)$.

Considérons la courbe Γ représentant géométriquement $F(\theta)$. θ est porté en abscisse, $F(\theta)$ en ordonnée. Soit M le point (θ, F). Pour une valeur déterminée de θ, la fonction $R(\theta,u)$ est continue en u, quel que soit u, pourvu que l'on pose $R(\theta,0) = f(\theta)$. Soit $\psi(\theta)$ le maximum de $|R(\theta,u)|$ pour toutes les valeurs de u. D'après

$$R(\theta, u) = \frac{Q[\theta, u] - Q[\theta, -u]}{u},$$

nous avons, quel que soit u :

$$|Q(\theta, u) - Q(\theta, -u)| < \psi(\theta)|u|.$$

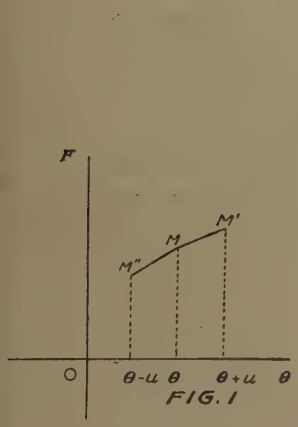


FIG. 1

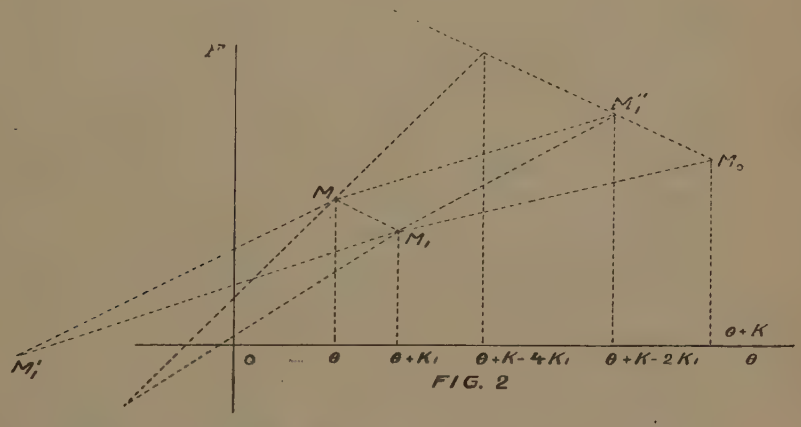


FIG. 2

Donc les points M' et M'' d'abscisses respectives $\theta + u$ et $\theta - u$ sont sensiblement alignés avec le point M. Les deux droites MM', MM' ont des pentes d'autant plus voisines l'une de l'autre que $|u|$ est plus petit (Fig. 1).

Donc de la position de M' d'abscisse $\theta + u$, nous déduirons avec une certaine approximation connue, la position de M' d'abscisse $\theta - u$. Sur l'axe des θ, nous pouvons considérer $\theta - u$ comme l'image de $\theta + u$ par rapport au point θ, regardé comme réfléchissant. M'' est sensiblement le symétrique de M' par rapport à M.

Considérons maintenant deux points M et M_1 de la courbe Γ, ayant pour abscisses $\theta, \theta + k_1$. Soit A un nombre supérieur à

$\psi(\theta)$ et à $\psi(\theta + k_1)$. Désignons par M_0 un autre point de la courbe, et soit $\theta + k$ son abscisse.

Formons sur l'axe des θ, les images du point $\theta + k$, par une succession de réflexions alternées sur les points-miroirs $(\theta, \theta + k_1)$. Nous obtenons, selon que la première réflexion a lieu sur θ ou sur $\theta + k_1$, deux suites de points-images :

$$\theta - k, \qquad \theta + k + 2k_1, \quad \theta - k - 2k_1, \quad \theta + k + 4k_1, \ldots$$

et

$$\theta - k + 2k_1, \quad \theta + k - 2k_1, \quad \theta - k + 4k_1, \quad \theta + k - 4k_1, \ldots$$

Les points représentatifs de F pour ces deux suites d'abscisses, seront, avec une certaine approximation que notre objet est d'étudier, 1° dans le premier cas, le symétrique M' de M_0 par rapport à M, puis le symétrique M'' de M' par rapport à M_1, puis le symétrique de M'' par rapport à M_1, et ainsi de suite, 2° dans le second cas, le symétrique M'_1 de M_0 par rapport à M_1, puis le symétrique M''_1 de M'_1 par rapport à M, etc.

Dans ce qui suit, nous ne restreindrons pas la portée de nos conclusions en considérant uniquement les points-images déduits de $\theta + k$ par un nombre pair de réflexions sur le couple $(\theta, \theta + k_1)$. Ces points-images ont pour abscisses des nombres en progression arithmétique de raison $2k_1$, formant la suite $\theta + k + 2mk_1$, m étant un entier de signe quelconque. Un tel point-image est obtenu par $|m|$ réflexions doubles de $\theta + k$ sur le couple $(\theta, \theta + k_1)$, la première réflexion se faisant sur θ ou sur $\theta + k_1$, selon que m est positif ou négatif. Exprimons les ordonnées des points de la courbe Γ correspondant aux points-images : $\theta + k + 2mk_1$.

Nous avons par hypothèse, quel que soit u :

$$F(\theta + u) + F(\theta - u) = 2F(\theta) + \sigma A u^2 \qquad \sigma^2 < 1$$

$$F[\theta - u] + F(\theta + 2k_1 + u) = 2F(\theta + k_1) + \sigma' A (u + k_1)^2 \qquad \sigma'^2 < 1$$

D'où :

$$F[\theta + u] - F[\theta + 2k_1 + u] = -2[F(\theta + k_1) - F(\theta)] + \sigma A[u^2 + (u + k_1)^2]$$

Supposons d'abord m positif. Donnons à u successivement les valeurs $k, k + 2k_1, \ldots, k + 2(m - 1)k_1$. Il vient :

$$F[\theta + k] - F(\theta + 2mk_1 + k) = -2m[F(\theta + k_1) - F(\theta)] + \sigma A\omega,$$

avec

$$\omega = k^2 + (k + k_1)^2 + \ldots [k + (2m - 1)k_1]^2.$$

Supposons m négatif et égal à $-m'$. Dans la relation précédente, nous remplaçons m par m' et k par $k - 2m'k_1$. Il vient :

$$F(\theta + k) - F(\theta + 2mk_1 + k) = -2m[F(\theta + k_1) - F(\theta)] + \sigma A\omega_1.$$

avec

$$\omega_1 = (k - k_1)^2 + \ldots + (k + 2mk_1)^2.$$

Les deux formules coïncident indépendamment de m, sauf par les coefficients ω et ω_1. Si $m=0$, on a $\omega=\omega_1=0$.

Nous écrivons ainsi la relation générale :

$$\frac{F(\theta+k)-F(\theta)}{k}=\frac{F(\theta+2mk_1+k)-F(\theta)}{2mk_1+k}\cdot\frac{2mk_1+k}{k}+$$
$$+\frac{F(\theta+k_1)-F(\theta)}{k_1}\times\frac{-2mk_1}{k}+\delta A\frac{\omega'}{k}$$

ω' étant ω ou ω_1 selon que m est positif ou négatif. Posons

$$k+2mk_1=k'$$
$$\frac{k'}{k}=\mu,\qquad\frac{-2mk_1}{k}=\nu.$$

Il vient :

$$Q[\theta,k]=Q[\theta,k']\mu+Q[\theta,k_1]\nu+\delta A\frac{\omega'}{k}.$$

Soit $\left|\frac{k}{k_1}\right|=r$ supposé au moins égal à 1, et ε défini par

$$\varepsilon^2=1,\quad\varepsilon\frac{k}{k}>0.$$

Nous choisirons l'image k' d'abord de manière que μ soit positif et ν non négatif. D'après $\mu+\nu=1$, cette condition sera

$$0\leq\frac{-2mk_1}{k}<1.$$

Donc m a le signe de $-\varepsilon$, si $m\neq 0$, et en outre $2|m|<r$. Donc,

si $\varepsilon=+1$, $-r<2m<0$, $\omega'=\omega_1=k^2\left[\left(1-\frac{1}{r}\right)^2+\ldots+\left(1+\frac{2m}{r}\right)^2\right]<2|m|k^2$

si $\varepsilon=+1$, $r>2m>0$, $\omega'=\omega=k^2\left[1+\left(1-\frac{1}{r}\right)+\ldots+\left(1-\frac{2m-1}{r}\right)^2\right]<2mk^2$.

Donc, dans tous les cas,

$\delta A\frac{\omega'}{k}$ peut être remplacé par $2\delta mkA$.

La substitution est exacte même pour $m=0$.

La condition $\mu>0$, montre que k' et k sont de même signe. Parmi toutes les images $\theta+k+2mk_1$ de $\theta+k$, situées du même côté de θ que $\theta+k$, choisissons celle qui, sans être intérieure à l'intervalle $\theta-k_1$, $\theta+k_1$, est la plus voisine de θ.

Nous appellerons ce point $0+k'$ *l'image-réduite propre à 0* du point $\theta+k$ par rapport au couple $(\theta,\ \theta+k_1)$. La distance de deux images consécutives obtenue par une suite de réflexions doubles sur le couple $(\theta,\ \theta+k_1)$ étant $2k_1$, k' vérifie les conditions

$$|k_1| \leq |k'| < 3\ k_1,$$

qui, jointes aux formules $k' = k + 2mk_1$ et à la condition $\frac{k'}{k} > 0$, déterminent complètement k'. En effet, soit p l'entier non négatif déterminé par les conditions

$$2p + 1 \leq r < 2p + 3.$$

D'après $\frac{k}{k_1} = \varepsilon r$ avec $\varepsilon^2 = 1$, $m\varepsilon \leq 0$ et $r > 2|m|$, on a : $\varepsilon \frac{k'}{k_1} = r - 2|m|$.

D'où $1 \leq r - 2|m| < 3$ et enfin $|m| = p$, $m = -p\varepsilon$.

$\theta + k'$ étant l'image-réduite caractérisée comme il est dit, nous trouvons finalement, en utilisant $2|m| < r = \left|\frac{k}{k_1}\right|$ la formule:

$$Q(\theta, k) = Q(\theta, k')\,\mu + Q(\theta, k_1)\,\nu + \delta \frac{k^2}{k_1} A \quad . \quad . \quad . \quad . \quad (4)$$

$$\text{avec } \delta^2 < 1, \text{ si } 0 < \frac{k'}{k} < 1, \ \delta = 0 \text{ si } k' = k.$$

Il est essentiel de noter que $0 < \mu = \frac{k'}{k}$, $0 \leq \nu$, $\mu + \nu = 1$. Ces propriétés et la formule (4) seraient conservées si k' était remplacé par l'un quelconque des termes de la série $k + 2qk_1$ compris entre k et k'. Mais il est essentiel pour la suite, que le rapport $\left|\frac{k'}{k_1}\right|$ soit compris entre deux nombres positifs fixes. Il nous sera commode d'avoir choisi pour jouer ce rôle les nombres 1 et 3.

Considérons maintenant une suite $h_1, h_2, \ldots, h_n, \ldots$ de nombres de signes quelconques, décroissant en modules et tendant vers 0, tels enfin que $\psi[\theta + h_n] < A$, A étant indépendant de n, avec en outre $\psi(\theta) < A$.

Cette hypothèse sur les h_n ne serait d'ailleurs pas rigoureusement indispensable pour valider le raisonnement et la conclusion ci-après.

En effet, désignons par $\psi[\theta, \eta]$ le maximum de $|R(\theta, u)|$ pour $|u| \leq \eta$, θ demeurant fixe. Le raisonnement subsiste alors moyennant la simple hypothèse

$$\psi[\theta + h_{n+1}, \quad 3|h_n|] < A.$$

Soit h un nombre dont la valeur absolue est au moins égale à h_1. Soit h' l'image-réduite, propre à θ, du point $\theta + h$ par rapport au couple $(\theta, \theta + h_1)$. On a:

$$Q[\theta, h] = Q[\theta, h']\,\lambda' + Q[\theta, h_1]\,\lambda_1 + \delta \frac{h^2}{h_1} A$$

avec

$$0 < \lambda' \quad , \quad 0 \leq \lambda_1 \quad , \quad \lambda' + \lambda_1 = 1 \quad , \quad \delta^2 < 1.$$

Transformons de même $Q[\theta, h']$ et $Q[\theta, h_1]$ grâce à $\theta + h_2$.

Soient respectivement $\theta + h''$ et $\theta + h'_1$, les images-réduites propres à θ, des points $\theta + h'$, $\theta + h_1$ par rapport au couple $(\theta, \theta + h_2)$. On a:

$$Q[\theta, h] = Q[\theta, h''] \mu'' + Q[\theta, h_2] \nu'' + \delta \frac{h'^2}{h_2} A$$

$$Q[\theta, h_1] = Q[\theta, h'_1] \mu'_1 + Q[\theta, h_2] \nu'_1 + \delta \frac{h_1^2}{h_2} A .$$

avec

$$0 < \mu'', \mu'_1 \quad ; \quad 0 \leq \nu'', \nu'_1 \quad ; \quad \mu'' + \nu'' = \mu'_1 + \nu'_1 = 1.$$

Donc

$$Q[\theta, h] = Q[\theta, h''] \lambda'' + Q[\theta, h'_1] \lambda'_1 + Q[\theta, h_2] \lambda_2 + \delta A \left[\frac{h^2}{|h_1|} + \frac{\lambda' h'^2 + \lambda_1 h_1^2}{|h_2|} \right]$$

avec

$$\lambda'' = \lambda' \mu'' \quad , \quad \lambda'_1 = \lambda_1 \mu'_1 \quad , \quad \lambda_2 = \lambda' \nu'' + \lambda_1 \nu'_1 .$$

Donc

$$0 < \lambda'', \qquad 0 \leq \lambda'_1, \qquad 0 \leq \lambda_2, \qquad \lambda'' + \lambda'_1 + \lambda_2 = 1.$$

Enfin d'après $h'^2 < 9 h_1^2$, $\lambda' + \lambda_1 = 1$, le coefficient de δA peut se remplacer *a fortiori* par $9 \delta A \left(\frac{h^2}{|h_1|} + \frac{h_1^2}{|h_2|} \right)$.

La méthode de transformation de $Q[\theta, h]$ est évidente. Nous définissons la suite h, h', h'', ..., $h^{(n)}$, ... par cette condition que $\theta + h^{(n)}$ est l'image-réduite propre à θ de $\theta + h^{(n-1)}$ par rapport au couple $(\theta, \theta + h_n)$. De même, $h_p^{(i)}$ n'existant pas pour $i < p$ et $h_p^{(p)}$ étant égal à h_p par convention, la suite $h_p^{(n)}$, constituée de nombres de mêmes signes, sera définie, pour $n > p$, par la condition que $\theta + h_p^{(n)}$ est l'image-réduite propre à θ, de $\theta + h_p^{(n-1)}$ par rapport au couple $(\theta, \theta + h_n)$. On aura des relations telles que les suivantes :

$$|h_n| \leq |h_p^{(n)}| < 3 |h_n|,$$

quel que soit $p \leq n$;

$$Q[\theta, h_p^{(n-1)}] = Q[\theta, h_p^{(n)}] \mu_p^{(n)} + Q[\theta, h_n] \nu_p^{(n)} + \delta_p^{(n)} A \frac{(h_p^{(n-1)})^2}{h_n}$$

avec

$$0 < \mu_p^{(n)} \ , \ 0 \leq \nu_p^{(n)} \ , \ \mu_p^{(n)} + \nu_p^{(n)} = 1 \ . \ . \ .$$

Le coefficient de $\delta_p^{(n)} A$ peut *a fortiori* être remplacé par $\frac{9 h^2{}_{n-1}}{h_n}$.

Cette relation permet de justifier par récurrence la formule

$$Q(\theta, h) = Q[\theta, h^{(n)}] \lambda^{(n)} + \ldots + Q[\theta, h_p^{(n)}] \lambda_p^{(n)} + \ldots + Q[\theta + h_n] \lambda_n + \left. \right.$$

$$+ 9 \delta A \left[\frac{h^2}{|h_1|} + \frac{h_1^2}{|h_2|} + \ldots + \frac{h^2{}_{n-1}}{|h_n|} \right] \qquad (5)$$

avec la condition qu'aucun des $\lambda_p^{(n)}$ n'est négatif et que leur somme pour $p = 0,1 \ldots, n$ est 1.

$$[\lambda_0^{(n)} = \lambda^{(n)}, \quad \lambda_n^{(n)} = \lambda_n].$$

Utilisons maintenant la propriété de la convergence uniforme vers 0 de la différence $Q[\theta, \lambda u] - Q[\theta, u]$ quand λ et $\frac{1}{\lambda}$ sont bornés, u tendant vers 0.

Soit $\varepsilon(\alpha)$ le maximum de la valeur absolue de cette différence, quand $1 \leq |\lambda| < 3$, $|u| < \alpha$, θ quelconque. Alors,

$$Q[\theta, h_i^{(n)}] = Q[\theta, h_n] + \sigma_{i.n}\, \varepsilon [|h_n|].$$

Les $\lambda_i^{(n)}$ étant non négatifs, on a:

$$|\Sigma \lambda_i^{(n)} \sigma_{i.n}| \leq \Sigma \lambda_i^{(n)} = 1.$$

Donc

$$Q[\theta, h] = Q[\theta, h_n] + \sigma' \varepsilon [|h_n|] + 9\, \sigma A \left[\frac{h^2}{|h_1|} + \ldots + \frac{h^2_{n-1}}{|h_n|} \right] . \quad . \quad (6)$$

Supposons que la série $\frac{h_n^2}{h_{n+1}}$ *soit absolument convergente.*

Nous allons déduire immédiatement de la formule (6) que $Q[\theta, h]$ tend vers une limite quand h tend vers 0.

Soit en effet m l'entier défini par

$$|h_m| < |h| \leq |h_{m-1}|.$$

Nous appliquons la formule (6) à la suite h, h_m, $h_{m+1}, \ldots, h_{m+q}$.

Dans le coefficient de $9\,\delta A$, nous remplaçons h^2 par h^2_{m-1}, et nous ajoutons tous les termes marquants de la série $\frac{h_n^2}{|h^{n+1}|}$. Nous obtenons *a fortiori*:

$$Q[\theta, h] = Q[\theta, h_{m+q}] + \sigma' \varepsilon [|h_{m+q}|] + 9\, \sigma' A \sum_{m-1}^{\infty} \frac{h_n^2}{|h_{n+1}|} \quad . \quad (7)$$

Soit h' un nombre quelconque inférieur en valeur absolue à h_{m-1} et q assez grand pour que $|h_{m+q}| < |h'|$. Nous trouvons, en faisant croître q:

$$|Q[\theta, h) - Q(\theta, h')| \leq 18 A \sum_{m-1}^{\infty} \frac{h_n^2}{|h_{n+1}|}.$$

Sous la seule condition: $|h|$ et $|h'| < |h_{m-1}|$.

Donc $Q[\theta, h]$ tend vers une limite quand h tend vers 0. $F(\theta)$ *possède une dérivée au point* θ. Soit $\varphi(\theta)$ sa valeur. On a, en faisant croître q indéfiniment dans la formule (7) *pour* $|h| < 2\alpha |h_1|$.

$$Q(\theta, h) = \varphi(\theta) + \sigma A \left[\frac{h^2}{|h_m|} + 9 \sum_{m}^{\infty} \frac{h_n^2}{|h_{n+1}|} \right] . \quad . \quad . \quad . \quad (8)$$

En résumé, *si* $|h_n|$ *tend vers* 0 *en décroissant, si la série* $\frac{h_n^2}{h_{n+1}}$

est absolument convergente, si les nombres $\frac{F(t+u)+F(t-u)-2F(t)}{u^2}$ *où* $t=\theta+h_n$ *restent bornés pour toute valeur réelle de u et pour toute valeur entière de n (positif), sous ces conditions suffisantes,* $F(\theta)$ *possède une dérivée au point* θ.

Un cas particulier remarquable est celui où la suite $\frac{h_n}{h_{n+1}}$ est bornée. Soit $\left|\frac{h_n}{h_{n+1}}\right| < \alpha$, α étant indépendant de n. Si $\frac{h_n}{h_{n+q}} < 2$, et si nous supprimons dans la suite les termes $h_{n+1}, \ldots, h_{n+q}$, la nouvelle suite obtenue h_n' satisfait à la condition $\left|\frac{h'_n}{h'_{n+1}}\right| < 2\alpha$. $|h|$ étant compris entre $|h_{m-1}|$ et $|h_m|$, nous considérons la suite h, h_m, $h_{m+1}, \ldots$, et, conservant son premier terme, nous la réduisons de proche en proche, en y supprimant, au fur et à mesure que nous en rencontrons un dans la suite parcourue dans son ordre naturel, tout terme supérieur en valeur absolue à la moitié du dernier terme conservé.

Dans la suite restante, h, $h'_1, h'_2 \ldots, h'_q, \ldots$ le rapport de chaque terme au suivant est inférieur en valeur absolue à 2α. La série $\frac{h'^2_n}{h'_{n+1}}$ est convergente, d'après:

$$|h'_n| < \frac{1}{2^n} \cdot |h|, \text{ et } \frac{h'^2_n}{|h'_{n+1}|} < 2\alpha\,|h'_n|.$$

On a:

$$\frac{h^2}{|h'_1|} + 9\sum_1^\infty \frac{h'^2_n}{|h'_{n+1}|} < 2\alpha\,|h|\left[1+\frac{9}{2}+\ldots+\frac{9}{2^n}+\ldots\right] = 20\alpha\,|h|,$$

Donc, *dans le cas où le rapport* $\frac{h_n}{h_{n+1}}$ *est inférieur en valeur absolue à un nombre* α *indépendant de n, et où le rapport* $|R(t,u)|$ *est borné par A quels que soient u réel et* $t=\theta+h_n$ *ou* $t=\theta$, $F(\theta)$ *possède une dérivée* $\varphi(\theta)$ *au point* θ, *et on a la formule* $Q[\theta,h] = \varphi(\theta) + 20\delta\,\alpha A h$, *pour* $|h| < 2\alpha\,|h_1|$. $(\delta^2 < 1)$ . . . (9)

Mathematics. "*Graphical Determination of the Moments of Transition of an Elastically Supported, Statically Indeterminate Beam*". II. By Prof. C. B. BIEZENO. (Communicated by Prof. J. CARDINAAL).

(Communicated at the meeting of December 29, 1917).

12. In quite the same way as it has been attempted in § 8 to prepare a transition from the case of three points of support to that of four, it might now be tried to use the construction just found for the treatment of the beam on five points of support, by cutting it above its last point of support but one and charging it there by a moment of 0, 1, 2, . . . metretons. We are, however, arrested by two difficulties. In the first place the amount of drawing required becomes so extensive, that it is impossible to avoid mistakes. In the second place, however, an obstacle arises which has not yet been able to manifest itself in the case of the beam on three or four points of support.

When the beam has been cut above the fourth point of support, it is among others necessary to construct a link-polygon for the left-hand part on four points of support after applying a moment of transition of one metreton above the last point of support.

In the construction, however, of this link-polygon the beam on four points of support is again cut above the third point of support. Consequently this will be charged besides by the given forces acting on ABC, by a force of $\frac{1}{L}$ ton, directed upward and originating from the introduced unit couple M_D.

Of course a similar thing happened in the case of the beam on four points of support above the second point of support. But there the ascent $\frac{\mu}{L}$ of the second point of support, due to the extra force, was known, because the remaining lefthand part of the beam was only supported at two points. Here the ascent of the third point of support is not known, as the unaltered lefthand part of the beam is itself statically indeterminate.

And although it would of course be possible by the aid of §§ 3—7 to determine the ascent which the righthand end of the beam ABC supported at three points, would be subject to in consequence of a

force acting at this extremity, the execution of the required construction would only increase the difficulty mentioned at the beginning of this §.

Yet all the auxiliaries for a fit construction of the elastic link-polygon of a beam on five or more points of support have been provided, as will appear from the following.

13. *Beam on more than four points of support.*

Let the beam on n points of support $A, B, C, \ldots U, V, W$, be given, and let it for the present be required to determine the descent and the inclination at the last point of support W, when the beam is successively charged at W by a unit force and a unit moment. Then the experience gained in the preceding §§ leads to the expectation that the quantities in question only depend upon the corresponding ones for the beam $A, B, C, \ldots U, V$, i. e. upon the descent and the inclination which will appear at the last point of support of the beam $A, B, C, \ldots U, V$, when in V a unit force, resp. a unit moment, acts.

Let us suppose these latter quantities, which may be indicated by y_{n-2}, φ_{n-2}, $\overline{y}_{n-2}$, $\overline{\varphi}_{n-2}$, for a moment to be known, and let us attempt to derive from them the y_{n-1}, φ_{n-1}, $\overline{y}_{n-1}$, $\overline{\varphi}_{n-1}$ required. In determining each of these quantities we might again use the introduction of different moments of transition M_V above V.

For each moment of transition M_V it would be necessary to determine the situation of the point W in two ways:

1. by the aid of the equations of equilibrium of the field VW to the right, supposed to be free, by means of which a point W is found;

2. by means of an elastic link-polygon belonging to the beam $A, B, C, \ldots U, V, W$, which gives a point $\overline{W}$.

If then the series of points $\overline{W}$ and W should appear to be similar, it would be possible to construct their double point, i.e. the extreme point of the link-polygon determining the required quantities.

If the line of action described really causes y_{n-1}, φ_{n-1}, $\overline{y}_{n-1}$, $\overline{\varphi}_{n-1}$ to be found, we must accordingly attempt to determine the corresponding quantities of the beam $ABC \ldots UV$ on $(n-1)$ points of support.

But this would be possible if under the same conditions of charge the inclination and descent were known for the beam $ABC \ldots U\delta$ on $(n-2)$ points of support.

On arguing further in this way, we are driven back to the beam

on two points of support, and it is therefore necessary first to find the quantities in question for this beam.

14*a*. With a view to this let us consider the freely supported beam AB charged at its right end by a force of one ton (fig. 3*a*). The descent $B\,{}_{1T}B$[1]) $= y_1$ as well as the angle of inclination φ_1 is

Fig. 3*a*.

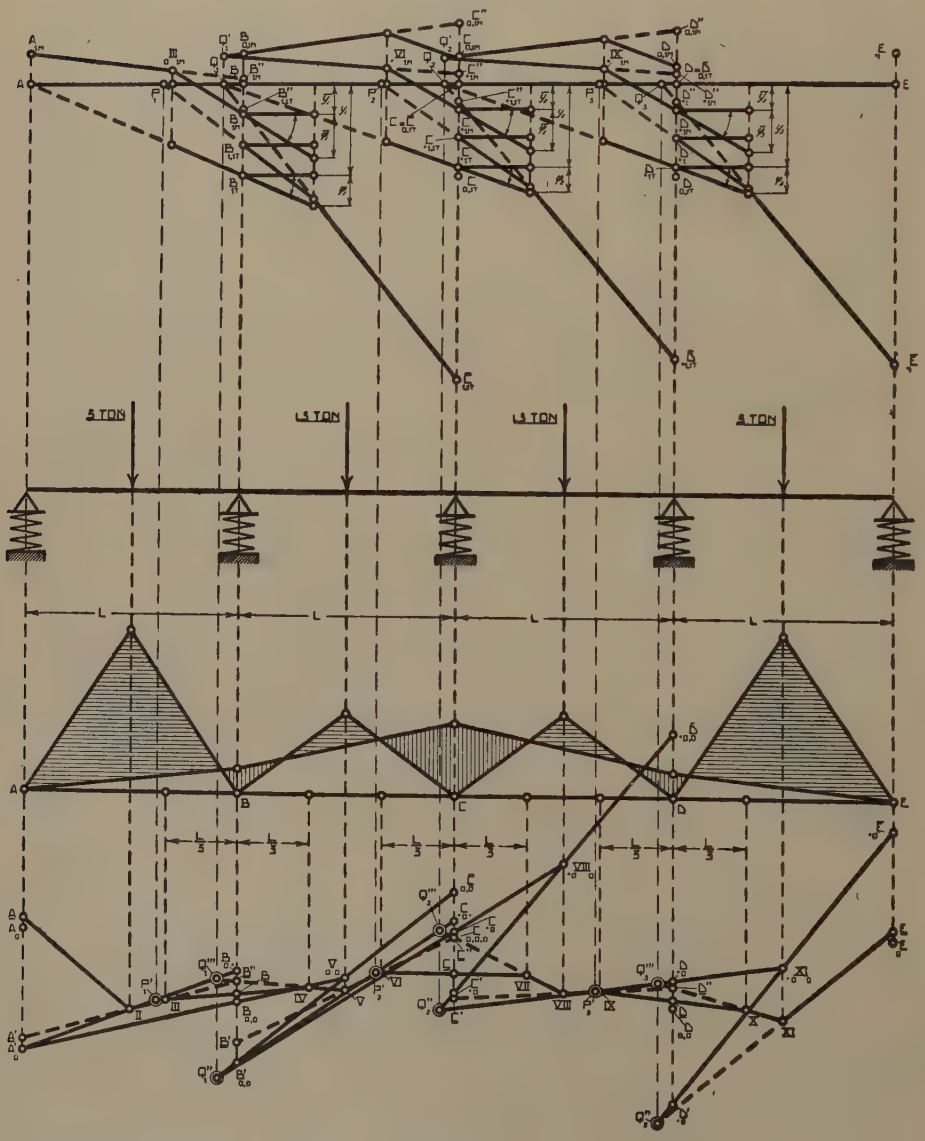


Fig. 3*b*.

[1]) In order to distinguish it from a moment of transition, a unit charge acting in a point of support $B, C \ldots$ is indicated by indices $1T$ or $1M$ placed under the letters $B, C \ldots$ according as it represents a force or a couple.

immediately known, as the point A remains in its place and AB remains straight. [1])

14*b*. If the end B is charged by a moment of 1 metreton, the point A rises by an amount AA_{1M}, while the point B descends by an amount $\underset{1M}{BB}$. As the sides $A_{1M}\ 3_{1M}$ and $3_{1M}\ \underset{1M}{B}$ must cut a segment of known length from $\underset{B}{l}$, the former, hence also the latter, is known.

Consequently the angle of inclination $(\bar{\varphi}_1)$ and the descent $(\bar{y}_1)$ at B can also for this charge be found in a very simple way.

15*a*. We can now proceed to the treatment of the beam ABC charged at its extremity C by 1 ton.

If the beam is cut above B, the point C descends by an amount $\underset{0\,1T}{C\,C} = \mu$. The beam AB remains uncharged. The construction of the elastic link-polygon furnishes therefore the straight line ABC; the point $\underset{0\,1T}{\bar{C}}$ coincides with C.

If then a moment of transition of 1 metreton is introduced at B, the point $\underset{0,1T}{C}$ rises by an amount $\underset{0,1T}{C}\ \underset{1,1T}{C} = \frac{l'}{L}$, so that $\underset{1,1T}{C}$ is known.

No more does the construction of $\underset{1,1T}{\bar{C}}$ by the aid of the elastic link-polygon give rise to difficulties. The introduction of the moment of 1 metreton above B will cause the point of support B to descend by an amount $\underset{1,1T}{B}\ \underset{1,1T}{B} = \bar{y}_1 + \frac{1}{L} y_1$, while the side III $\underset{1,1T}{B}$ assumes an angle of inclination $\bar{\varphi}_1 + \frac{1}{L}\varphi_1$.

The side $\mathrm{III}_1\ \underset{1,1T}{B}\ {}_1\mathrm{IV}_{1T}$ (indicated in fig. 3*a* by the line $P_1\ \underset{1,1T}{B}$) can therefore be drawn, hence, also the side ${}_1\mathrm{IV}_{1T}\ {}_1\underset{1T}{\bar{C}}$, since this side together with $\mathrm{III}_1\ {}_1\mathrm{IV}_{1T}$ must cut a segment of known length from l_B.

It is clear that the sides ${}_0\mathrm{III}_x\ {}_x\mathrm{IV}_{1T}$ belonging to the different moments of transition $M_B = x$ metretons, pass through one fixed point P_1 on AB, because the descents of the point $\underset{x\,1T}{B}$ as well as the angles of inclination of the side ${}_0\mathrm{III}_x\ {}_x\mathrm{IV}_{1T}$ increase in propor-

[1]) The angles of inclination φ are replaced in the usual way by their tangents. These tangents are read in fig. 3*a* on perpendiculars drawn at distance one to the right of the different points of support.

tion to x. The series of points $\underset{x\,1T}{B''}$ and ${}_{x}\mathrm{IV}_{1T}$ being moreover similar, also the joins $\underset{x\,1T}{B''}\ {}_{x}\mathrm{IV}_{1T}\ {}_{x}\overline{C}$ of corresponding points of these series pass through one fixed point Q_1, likewise situated on the line ABC.

The series of points $\underset{x.1T}{\overline{C}}$ and $\underset{x,1T}{C}$ are therefore similar.

Their double point at finite distance supplies the point $\underset{.1T}{C}$, while the line $\underset{.1T}{C}\ Q_1$ determines the angle of inclination in question.

15*b*. Also in the case of a charge of 1 metreton at C the beam is cut above B. In this case, however, the elastic support of B is charged by a force of $\frac{1}{L}$ ton. Consequently the point B rises by an amount $\frac{1}{L}y_1$ and the beam AB assumes at B an angle of inclination $\frac{1}{L}\varphi_1$. If for ABC a link-polygon is drawn on the supposition $M_B = 0$, the side $\mathrm{III}_0\ {}_{0}\mathrm{IV}_{1M}\ {}_{0}\mathrm{VI}_{1M}$ (indicated in the diagram by $\underset{0,1M}{B}\ \underset{0,1M}{C''}$), hence also the side ${}_{0}\mathrm{VI}_{1M}\ \underset{0,1M}{C_1}$ is fixed.

The point $\underset{0,1M}{C_1}$ conjugated to $\underset{0,1M}{\overline{C}}$ lies $\frac{1}{L}$ below C.

Now a second construction would be necessary for a moment of transition $M_B = 1$ metretons in order to construct, in addition to the pair of points $\underset{0,1M}{C_1}$, $\underset{0,1M}{\overline{C}}$ just found, a second, which would make possible the determination of the double point of the series $\underset{x1M}{C}$ and $\underset{x1M}{\overline{C}}$. The situation of this double point, however, depends exclusively upon the ratio $\frac{\overline{C}\ \overline{C}}{\underset{01M}{C}\ \underset{11M}{C}}$, which in its turn only depends upon the situation of the centres of rotation that appear to exist for the sides $\mathrm{III}_x, {}_{x}\mathrm{IV}_{1M}$ and ${}_{x}\mathrm{IV}_{1M}, {}_{x}\mathrm{VI}_{1M}$ and of which in the diagram only that of the sides ${}_{x}\mathrm{IV}_{1M}, {}_{x}\mathrm{VI}_{1M}$ has been indicated as Q'_1.

According to the reasoning of § 7 however, these points must lie perpendicularly above the points P_1 and Q_1.

The ratio in question has therefore already been found (fig. 3*a*) in the ratio $\frac{\overline{C}\ \overline{C}}{\underset{11T}{C}\ \underset{01T}{C}}$. Hence the double point $\underset{.1M}{C}$, when once $\underset{01M}{\overline{C}}$ and

C are known, can immediately be determined as well as the corre-
$_{01M}$
sponding point C''.
$_{.1M}$

The side $.IV_{1M}\,.VI_{1M}$ must lie along the line joining this point to Q'_1, so that the point $.VI_{1M}$ can be constructed. Then $.VI_{1M}\,C$ can
$_{.1M}$
be drawn, by means of which $\overline{y_2}$ and $\overline{\varphi_2}$ are found.

16. In quite the same way as $y_2, \overline{y_2}, \varphi_2, \overline{\varphi_2}$ have been determined out of $y_1, \overline{y_1}, \varphi_1, \overline{\varphi_1}$ also $y_3, \overline{y_3}, \varphi_3, \overline{\varphi_3}$ can be found out of $y_2, \overline{y_2}, \varphi_2, \overline{\varphi_2}$ and in general $y_n, \overline{y_n}, \varphi_n, \overline{\varphi_n}$ out of $y_{n-1}, \overline{y_{n-1}}, \varphi_{n-1}, \overline{\varphi_{n-1}}$.

Any new quadruple of unknowns belonging to a following point of support, requires the drawing after a fixed precept of only six lines.

Although for completeness' sake the construction of the point C
$_{.1M}$
has been discussed, it will not be necessary to execute it in reality.

For the theorem of MAXWELL teaches that $\overline{y_2} = \varphi_2$, so that C is
$_{.1M}$
directly determined.

17. By the aid of the quantities y, φ, $\overline{y}$ and $\overline{\varphi}$, to be found according to the §§ 14 and 15, the construction of the elastic link-polygon of the arbitrarily charged beam can now be executed in the way as has been indicated in fig. 3*b* for a beam on 5 points of support.

The charge is again applied in the middle of the fields, and amounts for the successive fields resp. to 3, $1^1/_2$, $1^1/_2$ and 3 tons.

First the descents $A\,A, B\,B, C\,C \ldots$ of the points of support are
$_{00}\quad _{000}\quad _{00}$
determined which appear when the beam is cut above all the points of support.

Then the point C is determined over which the beam ABC con-
$_{.0}$
sidered as a whole, must pass.

This point is determined exclusively by the aid of the link-polygon A', $\overline{C}$ conjugating the point C to the point C. For we can omit
$_{000}$ $_{00}$ $_{000}$
the construction of the link-polygon $A' \ldots B \ldots C$ because it is only
$_{01}\quad _{10}\quad _{10}$
used to determine two points $\overline{C}$ and C the situation of which gives
$_{100}\quad _{100}$
the ratio of the pieces into which the distance $\overline{C}\;C$ is divided by
$_{00}\;_{000}$
the point in question C. This ratio, however, is already fixed in
$_{.0}$

fig. 3a by $\frac{\overline{C}_{01T}\ \overline{C}_{11T}}{C_{01T}\ C_{11T}}$, for a reason mentioned before.

In an analogous way by the aid of the link-polygon $A \ldots \underset{.0}{C}$ VIII $\overline{\underset{0\ 00}{D}}$ the endpoint $\underset{.0}{D}$ is determined for the beam $ABCD$ considered as a whole. Of this polygon, belonging to the moment of transition $M_C = 0$, the side $Q''_1\ \underset{.0\ .0\ 0}{C}$ VIII and therewith VIII $\underset{.0\ 0\ .00}{\bar{D}}$ is determined. The situation of the double point $\underset{.0}{D}$ of the series of points $\underset{.y0}{\bar{D}}$ and $\underset{.y0}{D}$, which appear through the introduction of various moments of transition M_C and of which only the points $\underset{.00}{\bar{D}}$ and $\underset{.00}{D}$ are known, is again found with the ratio $\frac{\overline{D}_{01T}\ \overline{D}_{11T}}{D_{01T}\ D_{11T}}$, which appeared already in fig. 3a.

Finally $\underset{.0}{\bar{E}}$ is determined by the aid of the link-polygon $Q_2''\ \underset{.0\ .0\ 0}{D}$ XI, $\underset{.0}{\bar{E}}$, of which the extreme point $\underset{.0}{\bar{E}}$ forms together with $\underset{0}{E}$ a pair of points of the series $\underset{.z}{\bar{E}}$ and $\underset{.z}{E}$. The ratio in which the distance $\underset{.0\ .0}{\bar{E}\ E}$ must be divided by the required point E, has also been found already in fig. 3a by the ratio $\frac{E_{,\,.1}\bar{E}}{E_{,\,.1}E}$ by the introduction of a moment of 1 metreton above D.

The endpoint $\bar{E}$ of the link-polygon in question is therefore fixed, so that no more is necessary than to construct the polygon itself.

In the first place the side $\bar{E}$ XI can be drawn through Q'''_3, then XI X $\bar{D}''$ through Q'''_3, X IX through P_3' and IX VIII through D''. The last side cuts with VIII VII from l_B a piece of known length; hence VIII VII can also be drawn. This side cuts l_{Q_2}'' in a point Q_2''', which enables us to determine the point P_3' through which the side VII VI is to be drawn.

While the supposition was made that no moment of transition existed in D, the sides VI VII and VII VIII on the introduction of various moments of transition M_C had to rotate round fixed points P and Q, which were determined as the intersections of the lines l_{P_3} and l_{Q_2} with $Q_1''\ \underset{.0}{C}$. But the moment of transition in D influ-

ences the situation of the point $\underset{.0}{C}$. According to § 15 this point rises by an amount $\underset{.0}{C}\,\underset{0.}{C} = \frac{M_D}{L} y_2$, in consequence of which the line $\underset{.0}{Q_1''}\ \underset{.0}{\text{VIII}}$, which in absence of M_D contained the centres of rotation of the sides VI VII and VII VIII, must be replaced by the line $\underset{.0}{Q_1''}\ \underset{.0}{C}$. Now the point Q_2''' of this line is already determined as the intersection of $l_{Q_2''}$ with the side VIII VII, so that P_2', through which VII VI must pass, can be found as the intersection of $Q_1'' Q_2'''$ with l_{P_2}.

After VII VI we can draw VI V through C'', V VI being again determined by the known segment which VI V and V IV must cut from l_B.

Now V IV determines again on $l_{Q_1''}$ a point Q_1''' through which the line $A'_0 Q_1'''$ can be drawn, which intersects l_{P_1} in the point P_1' of the side IV III. The completion of the link-polygon does not present any difficulties.

18. It appears from the preceding considerations, as was indeed already noted in § 2, that with the beam on five points of support the subject mentioned in the title of this paper has been treated generally, save for the restrictions made, that the fieldlengths of the beam as well as the coefficients of stiffness of the elastic supports are supposed to be equal.

These restrictions, however, do not affect the general soundness of the construction.

If for instance the fieldlengths AB and BC (fig. 1) were unequal, the sides II III and IV V would indeed not meet on l_B, but at any rate on a perpendicular dividing the distance $l_{\text{III}}\ l_{\text{IV}}$ into pieces which are inversely proportional to the fieldlengths AB and BC.

Neither is the inequality of the coefficients of stiffness of the springs essential. If e. g. for the beam ABC with the fieldlengths $AB = L_1$ and $BC = L_2$ the coefficients of stiffness of the springs are α, β, γ, the extra descents of the springs which appear when the beam is cut above B in consequence of the introduction of a moment of transition of 1 metreton, will be $-\frac{\alpha}{L_1}, \frac{\beta}{L_1} + \frac{\beta}{L_2}, -\frac{\gamma}{L_2}$ instead of $-\frac{\mu}{L}\ 2\frac{\mu}{L}, -\frac{\mu}{L}$. This alters indeed the values of the segments $A'_0 A'_1$, $\underset{0}{B}\,\underset{1}{B}$, ${}_0C_1C$, but not essentially the construction itself.

When the beam is not prismatic as was assumed in § 1, but has a variable cross-section, the diagrams of bending moment can be reduced in the way already indicated by MOHR.

19. Lines of influence.

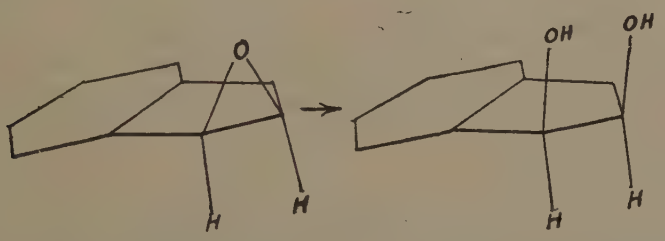
By the aid of the construction given in the preceding §§ the lines of influence for the moments of transition of a statically indeterminate elastically supported beam can now also be constructed graphically. In order to determine for instance the line of influence for the moment of transition above the p^{th} point of support, we need only construct the elastic line giving the position of the beam on being cut above the p^{th} point of support and charged in the arising cross-section by a moment of transition of 1 metreton. For each of the pieces into which the beam is divided, the moments of transition — hence the diagram of bending moment — can be determined as described, after which the elastic line can be drawn in the known way.

Chemistry. — *On the determination of the configuration of cyclic cis and trans diols and the rearrangements of atoms and groups of atoms during chemical reactions*". By Prof. J. BÖESEKEN and CHR. VAN LOON.

(Communicated at the meeting of June 28, 1919)

In former communications in which the configuration of the hydrindene diols was discussed, we called attention to the fact that *indene oxide*, when being hydrated, may yield the cis diol as well as the trans diol. In the meantime we ascertained that the quantities formed of these diols depend on the reaction of the medium, the formation of the trans compound is favoured by alkaline media.

Considering the probable situation of the atoms in indene oxide, the generation of trans diol deserves close attention; one might expect the cis compound:



Now it was of high importance to determine the configuration of the two diols with full certainty. Unfortunately the classic method, by testing the resolvability into optical antipodes, is of no avail here as both diols are asymmetric and consequently resolvable, so that another method had to be looked for.

We have already proved that of the two diols only one increases the conductivity of boric acid and we have deemed ourselves justified in assigning to this diol the cis configuration — rightly, as will be proved below.

[Here I may take it to be known, that the increase of the acid properties of boric acid by a number of substances, is due to the formation of complex dissociable compounds; these are formed especially if two hydroxyl groups are situated "favourably" in regard to boric acid.]

As this sole argument depends on the efficiency of the boric acid method, it called for a confirmation which could be given by our investigation on the *cyclapentane diols*.

For here we can verify the boric acid method by the classic one, as only the trans diol is not identical with its mirror image and consequently resolvable into optical antipodes.

We shall not enter here into details about the preparation of these diols; suffice it to state, that the one diol was prepared by hydrating *cyclopentene oxide*, while the other was obtained from cyclopentene by oxydation with $KMnO_4$.

The properties of the diols are as follows:

	mp.	bp.	m. p. of the diphenyl urethane	m. p. of the di-p. nitro-benzoate.
$C_5H_8(OH)_2$ from C_5H_8 and $KMnO_4$	29°—30°	123.9°/29	205°	117°—118°
$C_5H_8(OH)_2$ from C_5H_8O and H_2O	54°.5—55°	136°/21.5	221°	145°

In order to establish with certainty which of these two glycols was the cis and which the trans diol, they were treated with *l-menthyl-isocyanate*, in doing which the first one produced one single di-l-menthyl-urethane, while the highmelting diol yielded a mixture of di-l-menthylurethanes differing very much as regards rotatory power. Without isolating and saponifying these urethanes, we can draw the conclusion that here the urethanes of the trans diol were formed viz *d-trans-cyclopentane-diol-di-l-menthyl-urethane* and *l-trans-cyclopentane-diol-l-menthyl-urethane*.

From this however one must not conclude without further consideration that the diol with the higher melting point was in fact the trans diol. During the reaction of l-menthylisocyanate a sort of Walden inversion might have taken place

However a closer inspection renders this improbable in a high degree.

As we set forth in our last communication such an inversion is only to be expected when the reaction takes place at the atom which governs the configuration.

This is not the case here:

$$\equiv \underset{*}{C}—O—H \;+\; RNCO \;=\; \equiv \underset{*}{C}—O—\underset{\displaystyle RNH}{\underset{|}{CO}}$$

as the reaction takes place by detaching the O—H-linkage and so the typical C-atom is left alone [1]).

[1]) It is for this reason that we have not applied other methods for the resolution into optical antipodes (c.q. esterification with active acids), because then the entire OH-group may be eliminated, in which case the C-atom determining the asymmetry is attached.

We may therefore conclude with great certainty that the isomer with the higher melting point is the trans diol, the one with the lower melting point the cis diol.

Then the conduct of the two diols in relation to boric acid was studied.

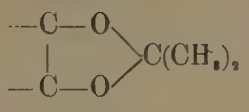
In effect it was found that the cis diol considerably augmented the conductivity of boric acid while the trans diol caused a small depreciation.

The boric acid method therefore proves to yield a positive result only in the case of the OH-groups being situated near to each other.

So now we can say with complete certainty that hydrindene diol (see former communication) m.p. 108°, which increases the conductivity of boric acid, is cis-hydrindene diol, while the one with the high melting point (159°) is the trans isomer without any doubt. The last substance exercises a small decrease of conductivity of boric acid.

By a communication of E. FISCHER (B. 28, 1146, 2496 (1895) on the ready formation of cyclic additional compounds of polyalcohols with aldehydes and ketones, one of us (CHR. VAN LOON.) has been incited to start an investigation about the conduct of these stereoisomeric diols in regard to acetone.

Here five- (or six) membered rings are formed of the following type :



Though not certain, it is however highly probable that with this condensation the decisive C-atoms are left alone so that here too a rearrangement in the sense of the WALDEN inversion is out of the question.

With surprising ease the expected condensation product was formed from cis hydrindene diol as well as from cis cyclopentane diol, while the trans-compounds under the same circumstances [the diols were set apart for 24 hours with a twenty-fold quantity of pure acetone containing 1 % HCl] remained absolutely unchanged.

We immediately made use of this method to have the configuration of the cyclohexane diols fixed.

These two compounds were obtained

1. by the action of potassium hydroxide on cyclohexene iodhydrin according to BRUNEL, during which action the oxide may be regarded as an intermediate product. — This diol melting at 104° was taken for the cis diol by BRUNEL, because it originated from the oxide.

2. by oxidation of cyclohexene with $KMnO_4$, by which a compound is formed melting at 99° and which was taken for the trans diol.

However as this last compound according to experiments executed by H. G. DERX, quantitatively yielded an acetone compound, we must assign to it the cis configuration; the diol, melting at 104°, did not react.

Curiously enough both exercise a small negative influence on the conductivity of boric acid, so that in this case the acetone method is more reliable than the boric acid method.

We must however observe that the classic method, based on the action of an active isocyanate has not yet been applied.

So with the cyclopentane diols the configuration has been determined in three ways entirely independent of each other; the reliability of the boric acid method has been greatly exhanced by this. A close study will have to be made of the acetone method. It has the great advantage of quickly leading to the purpose; however its drawback is, that under the influence of the condensation reagent (HCl) inversions are not impossible.

The determination of the configuration of the cyclic 1-2-diols has brought to light the remarkable fact that by the addition of water to the oxides not only the expected cis diol is formed, but besides and sometimes exclusively the trans-isomer.

Therefore, if the oxide has a configuration in which the oxygen atom lies outside the plane of the cyclopentane ring, which configuration in regard to the distribution of matter is the most probable one, then the opening of the three-membered ring must have been accompanied by an inversion.

It is remarkable that this inversion with the symmetrical oxides of cyclopentene and cyclohexene is almost complete and that under all circumstances; on the other side with the asymmetrical indene oxide the inversion is dependent on the reaction of the medium.

A very weak alkaline reaction reduces the quantity of cis diol, which is the principal product in acid medium, to zero.

Attention may be drawn to the fact, that with the reaction in alkaline medium, β hydrindone (or a condensation product there-of) is always formed, so that the alkali seems to loosen the α-CO-linking.

Indeenoxyd → β-hydrindon

As exactly in this case trans diol is formed and a Walden inversion cannot otherwise take place but at the atom which determines the stereoisomerism, it is very probable that the change of the configuration takes place at the α-C-atom.

A second observation may finally be made about the oxidation of cyclopentene and cyclohexene by $KMnO_4$. Thereby, principally at least, the cis diols appear to be formed. From this it follows that the oxides cannot be the intermediate products, as these would pass into trans diols under the circumstances of the experiment.

Perhaps the favoured production of the cis diols by $KMnO_4$ is related to the formation of complex compounds of trivalent manganese. For on the one side it appeared that oxidation of oxalic acid by $KMnO_4$ also commences with the formation of these manganese compounds, while on the other side it was found that the α-hydroxy-acids are very liable to forming complex manganese compounds. In these compounds the hydroxyl groups are favourably situated, as was shown by the determination of the conductivity of mixtures with boric acid. Then we should have to admit here that the possibility of the formation of these complex compounds with cis-diols would exercise an influence leading to their production.

However in that case a tendency to further oxidation of the cis diols is to be anticipated, just as the α-hydroxy acids are easily attached by mangani hydroxide.

This would then explain the very poor yields not surpassing 20%: a closer examination however will have to clear up this matter.

Chemistry. — *"On some Condensation-products of Aromatic Aldehydes and Amines."* By Prof. F. M. JAEGER.

(Communicated at the meeting of May 29, 1920).

§ 1. Although, according to HANTZSCH's and WERNER's theoretical views, the existence of stereoisomeric forms should be possible in the case of condensation-products of aromatic aldehydes and amines of the type: $R_1—CH=N—R_2$, yet it had appeared impossible during a long time to find with certainty [1]) cases of such isomerism with these so-called "bases of SCHIFF". In 1906, however, ANSELMINO [2]) described some cases, where substances of this kind were met with in two different crystalline modifications, which at the same time appeared to be strongly different in colour, being red and yellow. The author concluded from his investigations that no true *dimorphism* in the common sense of the word was present here, but that rather a chemical *isomerism* had to be supposed. The arguments brought to the fore by him for demonstrating that neither enantiotropic, nor monotropic relations whatsoever between the crystalforms of the red and yellow modifications of *o-oxy-m-methyl benzylidene-aniline* should be present, can, however, in our opinion hardly be estimated to be convincing. It seems notwithstanding this to be true, that the deviating chemical character of the yellow and the red forms, of which the last reacts much more easily with reagents attacking the *HO*-groups of the molecule, points in this case really to a chemical isomerism, in which to the red modification must then be attributed probably the *trans*-configuration, in the sense of WERNER's theory.

In the light of the interpretations given of the more recent investigations of crystals by means of RÖNTGENrays, the question about the discrimination between cases of "physical", in contrast with "chemical" isomerism, seems to have no longer any real significance, at least for solid matter: undoubtedly each modification of polymorphous substances will in the solid state also possess a definite spatial configuration differing from that of the other modification; and probably this difference will, at least partially, be preserved in the state of

[1]) A. HANTZSCH and O. SCHWAB, Ber. d. d. Chem. Gec., **34**, 8?2, (1901).

[2]) O. ANSELMINO, Ber. d. d Chem. Ges. **38**, 3989, (1906); **40**, 3465, (1907).

solution, and almost certainly in the molten mass. But only, if such differences be really stated in the liquid phases to a measurable

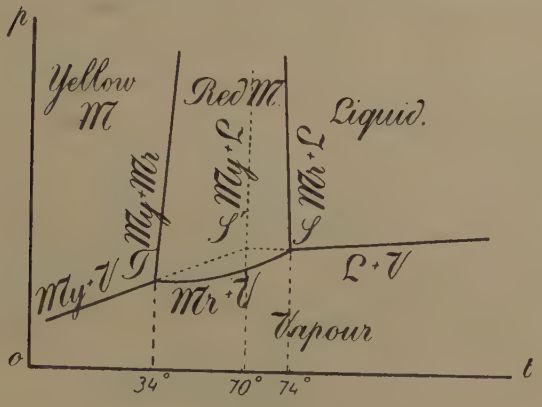


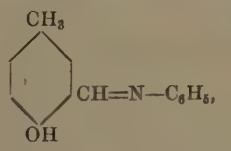
Fig. 1.

degree, it appears rational to speak of two kinds of chemical molecules.

However, disregarding for a moment their chemical isomerism, from a *crystallographical* point of view, the red and yellow modifications of the base mentioned, seem, in our opinion, to be related as true enantiotropic forms, as e.g. is the case with monoclinic and rhombic *sulphur*. The *ir*reversibility observed by ANSELMINO is evidently only an *apparent* one, caused by intensive retardation phenomena: the transition-temperature: yellow $\rightleftarrows$ red, is 34° C., while the meltingpoint of the red modification is found to be 74° C. and that of the (metastable) yellow form 70° C. By this interpretation all relations existing between the red and yellow forms, as observed by ANSELMINO, may be explained in an unambiguous way.

§ **2**. With respect to the crystallographical properties of these compounds, in the first place the numbers relating to the derivatives already obtained by ANSELMINO, may be recorded in the following. They were already obtained by us in 1906, but by special circumstances their publication has been postponed till now.

The condensation-product of *p-homosalicylaldehyde* (from *p-cresol*) and *aniline*: **o-oxy-m-methyl-benzylidene-aniline**:



occurs in two forms, of which the one is *yellow*, the other *red*, and which were studied already formerly by H. TRAUBE and F. SCHMELING[1])

[1]) F. SCHMELING, Diss. Greiswald, (1905), p. 56, 58.

in detail. The *yellow* (metastable) modification, melting at 70° C., is rhombic-bipyramidal, with the parameters: $a:b:c=0{,}3732:1:0{,}4228$, and the forms: {010}; {011}; {101}; {102}. Its birefringency is of positive character; the optical axial plane is parallel to {100}. The crystals show a cleavability parallel to {100} and {010}; their specific gravity at 17° C. is: $d_{4^\circ} = 1{,}243$, from which the equivalent-volume is calculated at: 169,75, and the topical parameters at: $\chi:\psi:\omega = 3{,}8269:10{,}2471:4{,}3322$.

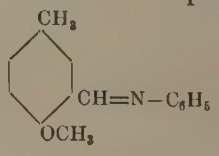
The *red* modification, which melts at 74° C., and to which the yellow form changes at 34° C., is monoclinic-prismatic. The parameters published by the author do *not* agree with those calculated from his angular values: they are really:

$$a:b:c = 0{,}2362:1:0{,}6579;$$
$$\beta = 74°9\tfrac{1}{2}',$$

if the same angles be used as by the author mentioned. The occurring forms have the symbols: {010}, {001}, {110}, and {011}. The optical axial plane of these strongly pleochroïtic, negatively birefringent crystals is perpendicular to {010}; the cleavage occurs parallel to {001} and {010}. The specific weight of the crystals is: 1,263 at 17° C.; the equivalent-volume is therefore: 167,06, and the topical parameters are calculated at: $\chi:\psi:\omega = 2{,}4511:10{,}3770:6{,}8271$. The transition of the yellow into the red crystals occurs in such a way, that the two modifications are rigorously orientated with respect to each other in two different ways, the faces of {010} of the two forms remaining always parallel to each other; — a fact clearly demonstrating the intimate relation of their internal structures. It is worth remarking here, that the dimensions in the direction of the *b*-axes in both modifications appear to be almost the same (namely: 10,3, as topical parameter), while the intergrowth of the *a*- and *β*-crystals parallel to {010} occurs in such a way that either the *c*-axis of the one modification coincides with the *c*-axis of the other, or the *a*- and *c*-axes of the crystals appear to be interchanged, although in these directions the topical parameters do not show a direct relation to each other.

§ 3. II. o-Methoxy-m-methyl-benzylidene-aniline.

This substance, which has the composition:



was obtained from the foregoing by means of methylsulphate at 40° C. It melts at 70° C., and crystallizes from ligroin in beautiful, pale yellow, transparent crystals.

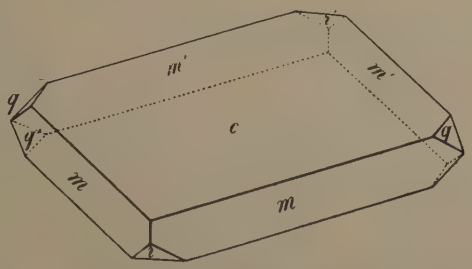


Fig. 2. *o-Methoxy-m-methyl-benzylidene-aniline.*

Monoclinic-prismatic.

$a : b : c = 1{,}2792 : 1 : 1{,}0509$;

$\beta = 76° 59\frac{1}{3}'$.

Forms observed: $c = \{001\}$, large and lustrous; $m = \{110\}$, yielding good reflexes, like $q = \{011\}$ also; $r = \{\bar{1}01\}$, small, but well determinable. The aspect of the crystals is tabular parallel $\{001\}$.

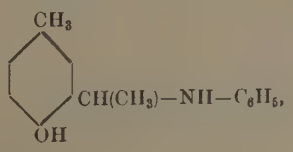
Angular values:	*Observed:*	*Calculated:*
$c : q = (001) : (011) =$*	45° 39′	—
$c : m = (001) : (110) =$*	81 54	—
$m : m = (110) : (1\bar{1}0) =$*	102 31	—
$c : r = (001) : (\bar{1}01) =$	44 22	44° 27′

No distinct cleavage was found.

The specific weight of the crystals at 16° C. was: 1,166; the molecular volume is therefore: 192,96, and the topical parameters are: $\chi : \psi : \omega = 6{,}7561 : 5{,}2813 : 5.5502$. The form-analogy with the red modification of the foregoing substance is undeniable.

§ 4. III. o-Oxy-m-methyl-α-anilido-ethylbenzene.

This compound, which melts at 90° C., was obtained from the first by means of two molecules of methylmagnesium-iodide in boiling etheric solution, and subsequent decomposition of the product with water. It has the formula:



and crystallizes from ligroin in very small, colourless, and almost rectangular plates.

Monoclinic-prismatic.

$a : b : c = 0{,}2682 : 1 : 0{,}7254.$

$\beta = 85° 47'.$

Forms observed: $b = \{010\}$, predominant; $m = \{110\}$ and $a = \{100\}$, well reflecting. In the zone of $q = \{011\}$, $s = \{012\}$ and $c = \{001\}$, the angular measurements ordinarily are not so accurate as in the other zones; commonly $q = \{011\}$ is the best developed. The aspect of the crystals is that of thin plates parallel to $\{010\}$.

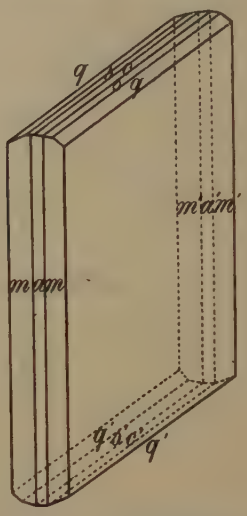


Fig. 3. *o-Oxy-m-methyl-α-anilido-ethylbenzene.*

Angular values:	*Observed*:		*Calculated*:	
$b : m = (010) : (110) =$	* 75°	1½′	—	
$b : q = (010) : (011) =$	* 54	7	—	
$a : q = (100) : (011) =$	* 86	35	—	
$a : c = (100) : (001) =$	86	1½	85°	47′
$s : q = (012) : (011) =$	15	56	16	0
$s : s = (012) : (0\bar{1}2) =$	40	3½	39	46½
$m : q = (110) : (011) =$	78	0	77	56
$m : a = (110) : (100) =$	14	58½	14	58½

A cleavage exists parallel to $\{001\}$.

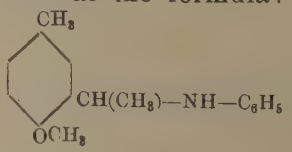
The specific weight of the crystals at 17° C. is: 1,107; the equivalent-volume therefore: 205,06. The topical parameters are: $\chi : \psi : \omega = 2{,}7319 : 10{,}1861 : 7{,}3890$.

On $\{010\}$ the extinction-angle is 43° with respect to the direction of the *c*-axis in the quadrant behind. Probably the optical axial plane is parallel to $\{010\}$.

§ 5. IV. o-Methoxy-m-methyl-α-anilido-ethylbenzene.

This substance was obtained from the corresponding benzylidene-aniline by means of methylmagnesium-iodide and subsequent decomposition by water.

The compound, which has the formula:



melts at 78° C., and crystallizes from ligroin in big, colourless, strongly refracting crystals of tabular or prismatic aspect. Ordinarily

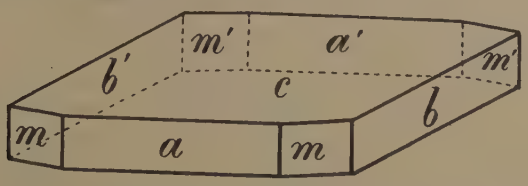


Fig. 4. *o-Methoxy-m-methyl-α-anilido-ethylbenzene.*

they manifest curved faces, exact measurements thus being rather difficult.

Rhombic-bipyramidal.

$a : b = 0{,}3301 : 1.$

Forms observed: $c = \{001\}$ predominant; $a = \{100\}$ and $b = \{010\}$, yielding good reflections; $m = \{110\}$, small, but lustrous.

Angular values:	*Observed*:		*Calculated*:
$a : m = (100) : (110) =$*	18°	16	—
$b : m = (010) : (110) =$	71	44	71° 44′

All other angles are 90°.

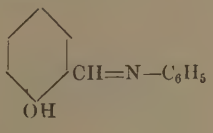
A good cleavage was found parallel to {100} and {010}.

The optical axial plane is {100}, with the *b*-axis as first bisector. The angle of the optical axes is very small, with extraordinarily strong dispersion: $\rho > v$; the apparent angle of the axes in oil ($n = 1{,}54$) was about 48° for the red, and about 25° for the violet rays. On {001} corrosion-figures were obtained of rectangular form, in agreement with the adopted crystallographical symmetry.

At 16° C. the specific of the crystals was: 1,098; the equivalent-volume therefore, being: 219,49.

§ 6. V. o-Oxy-benzylidene-aniline.[1])

This compound, having the formula:



[1]) Conf. also: L. Duparc, Ann. d. Chemie, **266**, 140 (1891); here *b* is taken as {001}, the axial ratio, therefore becoming: $c' : b' : a' = 4{,}586 : 1 : 2{,}1922$. (In Duparc's paper $a : b$ is erroneously taken ten times too small, and the *a*- and *c*-axes are interchanged. The crystals are identical with ours.

and melting at 50°,5 C., was obtained from salicylaldehyde and aniline.

The substance is *dimorphous*: it occurs in a less stable rhombic α-modification, and in a monoclinic β-form, which is obtained in most cases; both modifications are yellow.

1. *α-Modification.*

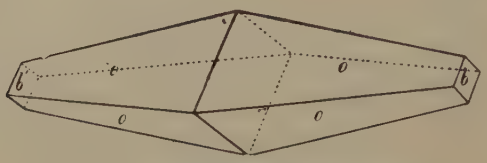


Fig. 5. *o-Oxy-benzylidene-aniline.*
(α-Modification).

From ligroin this modification crystallizes in most cases in the form of big, yellow, almost always opaque and flattened bipyramids.

Rhombic-bipyramidal.

$a : b : c = 0{,}4729 : 1 : 0{,}2188.$

Forms observed: $o = \{111\}$, big, but badly reflecting; $b = \{010\}$, small, yielding good reflexes. The crystals obtained from a solution in methyl-alcohol showed also a prism $m = \{130\}$, the faces of which gave good images.

Angular values:	*Observed:*	*Calculated:*
$o : o = (111) : (1\bar{1}1) =$	* 22°28½′	—
$o : o = (111) : (\bar{1}11) =$	* 48 39	—
$o : o = (111) : (11\bar{1}) =$	125 55	125°47′
$o : b = (111) : (010) =$	78 46	78 46
$m : b = (130) : (010) =$	34 59½	35 11

No distinct cleavage was found.

The specific weight of these crystals was: 1,087 at 16° C.; the equivalent-volume is thus: 181,23, and the topical parameters are calculated at: $\chi : \psi : \omega = 5{,}7005 : 12{,}0539 : 2{,}6375$.

2. *β-Modification.*

The crystals of the α-modification are easily transformed into those of the β-form by recrystallisation. If, however, the long needles of the β-modification thus obtained, are again recrystallized from methyl-alcohol, they are again changed into the bipyramids of the α-form.

Strongly refracting, yellow needles.

Monoclinic-prismatic.

$a : b = 2,4641 : 1$;

$\beta = 26° 2\frac{1}{2}'$

Forms observed: $m = \{110\}$, large and lustrous; $a = \{100\}$, narrower; $c = \{001\}$, well developed. Moreover, again a negative pyramid and a doma are observed, which, however, cannot be determined more precisely. It is for this reason, that the occurring face c was taken as $\{001\}$, although this form represents certainly not a basal face, but a horizontal prism.

Fig. 6. *o-Oxy-benzylidene-aniline. (β-Modification).*

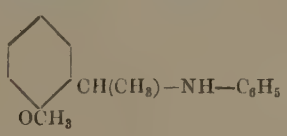
Angular values:	*Observed*:	*Calculated*:
$m : a = (110) : (100) =$	* 47° 15′	—
$a : c = (100) : (001) =$	* 26 2½	—
$m : c = (110) : (001) =$	52 40	52° 25′

No distinct cleavability was observed.

The specific weight of the crystals was: 1,184 at 17° C.; the molecular volume is, therefore, 166,38.

§ 7. VI. *α*-Anilido-ethyl-anisol.

This compound was prepared from the just mentioned by means of methylmagnesium-iodide, etc. It has the formula:



and melts at 46° C.

Fig. 7. *Anilido-ethyl-anisol.*

From ligroin badly developed, strongly refracting needles are deposited, which allow only approximate measurements.

Rhombic-bipyramidal.

$a : b : c = 0,884 : 1 : 0,465.$

Forms observed: $t = \{110\}$, $m = \{320\}$, $p = \{210\}$, and $n = \{520\}$, all about equally narrow, and yielding multiple reflexes; $q = \{011\}$, smaller, and badly reflecting. The aspect of the crystals is elongated in the direction of the c-axis.

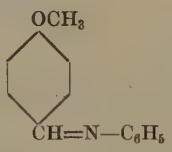
Angular values:	*Observed:*	*Calculated:*
$t:t = (110):(\bar{1}10) =$*	97° 4′	—
$q:q = (011):(0\bar{1}1) =$*	49 51	—
$t:m = (110):(320) =$	11 12	11° 0′
$m:p = (320):(210) =$	6 22	6 37
$p:n = (210):(520) =$	8 40	8 31

A distinct cleavability was not stated.

The specific weight of the crystals was: 1,141 at 18° C.; the equivalent-volume is thus: 176,16, and the topical axial ratios are calculated at $\chi:\psi:\omega = 6{,}6649:7{,}5395:3{,}5059$.

§ 8. VII. p-Methoxy-benzal-aniline (*Anisal-aniline*).

This substance, which melts at 63° C., and possesses the constitution:



was obtained from anisaldehyde and aniline.

It crystallizes from ligroin in colourless, well developed, very transparent crystals, having the odour of anisol.

Monoclinic-prismatic.

$$a:b:c = 1{,}5745:1:0{,}8063;$$
$$\beta = 65°21'$$

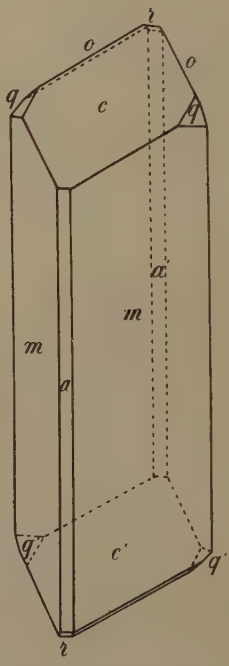


Fig. 8. *Methoxy-benzal-aniline.*

Forms observed: $c = \{001\}$, well developed and yielding splendid reflexes; $q = \{011\}$, $r = \{\bar{2}01\}$, and $o = \{\bar{2}11\}$, giving all sharp mirror-images; $m = \{110\}$ and $a = \{100\}$, somewhat narrower, but well measurable. The form a is often absent, or only developed with a single face, while o and r are often very narrow. The aspect of the crystals is that of thick prisms with an elongation parallel to the c-axis. They are generally well built.

Angular values:	*Observed:*	*Calculated:*
$c : a = (001) : (100) =$*	65° 21′	—
$c : q = (001) : (011) =$*	36 14	—
$m : m = (110) : (1\bar{1}0) =$*	110 6½	—
$c : r = (001) : (\bar{2}01) =$	58 30½	58° 23½
$o : r = (\bar{2}11) : (\bar{2}01) =$	33 57½	33 51
$m : q = (110) : (011) =$	47 18	47 22½
$o : m = (\bar{2}\bar{1}1) : (\bar{1}\bar{1}0) =$	44 7	43 54
$c : m = (001) : (110) =$	76 7½	76 10½
$m : q = (\bar{1}\bar{1}0) : (0\bar{1}1) =$	73 3	73 2¼

Perfect cleavable parallel to {001}.

An apparently second modification was, on more detailed investigation, really identical with the one described. However, yet another, truly polymorphic modification was observed [1]), crystallizing in extremely thin, unmeasurable, small plates with normal extinction; they are first deposited from solutions, but are rapidly changed into the crystals described in the above.

The needles here investigated, have oblique extinction: on m at an angle of 22½° with the direction of the c-axis.

The specific weight of the crystals at 17° C. was: 1,165; the equivalent-volume is thus: 181,11.

Topical parameters: $\chi : \psi : \omega = 8{,}4931 : 5{,}3942 : 4.3494$.

We are occupied with tentatives to obtain condensation-products of other aldehydes and amines of the aromatic series, with the purpose to find other cases of polymorphism or isomerism with bases of this kind. Perhaps we shall be able to return to this question within a not too remote future.

Laboratory for Inorganic and Physical Chemistry of the University.

Groningen, May 1920.

[1]) H. Ott, Monatshefte f. Chemie, **26**, 340 (1905).

Chemistry. — *"The Photochemical Decomposition of Potassium-cobaltioxalate and its Catalysis by Neutral Salts"* by Prof. F. M. JAEGER and G. BERGER.

(Communicated at the meeting of May 29, 1920).

§ 1. With the intention of studying the photochemical action of dextro- and laevogyratory circularly polarized light upon both optical antipodes[1]) of *potassium-cobalti-oxalate*: $K_3\{Co(C_2O_4)_3\} + 3\,H_2O$, and with the purpose of proving the probable difference in speed of reaction with each component, if attacked by circularly polarized light of opposite direction, — we started a series of experiments, which were of a preliminary character as regards the specific peculiarities of the photochemical process itself.

Simultaneously we tried to find out, if it would be possible to regulate the speed of reaction by the addition of certain substances to the solution in such a way that the velocity became as favourable as possible to the purpose aimed at on starting these experiments. We give already here a review of the results obtained, which must be considered as the foundation of further investigations, because we found some remarkable facts, which in their turn might be of interest as startingpoints to some other research-work of a more general character.

If all details are, for the moment, left aside, we can say that the photochemical decomposition of the complex *potassium-cobalti-oxalate* occurs in a way fully analogous to that observed in the case of the corresponding *ferric* salt of analogous constitution: in our case, *carbondioxide* is split off, and a pink coloured precipitate of *cobalto-oxalate*: CoC_2O_4 is formed, while a gradually increasing quantity of *potassium-oxalate* goes into solution; this last salt may, for a small part, combine with some *cobalto-oxalate* formed, into a complex salt of the constitution: $K_2\{Co(C_2O_4)_2\}$, which, however, is almost completely dissociated in its components.

The reaction may principally be formulated in the following way:

$$2\,\{CoC_2O_4\}, K_2 = 2\,CoC_2O_4 + 3\,K_2C_2O_4 + 2\,CO_2;$$

[1]) F. M. JAEGER, Receuil des Trav. des Chim. d. Pays-Bas, **38**, 247—256, (1919); *idem, Lectures on the Principle of Symmetry and its Applications in All Natural Sciences*, 2nd Edit., Amsterdam, (1920), p. 216, 249, 250, 317.

or, — if the electrolytic dissociation of these salts is taken into account, perhaps better by the relations:

$$2\,\{Co(C_2O_4)_3\}''' = 2\,\{Co(C_2O_4)_2\}'' + C_2O_4'' + 2\,CO_2,$$

and

$$\{Co(C_2O_4)_3\}''' \rightleftarrows Co'' + 2\,C_2O_4''.$$

§ 2. The photochemical reaction mentioned was, for the first time, studied systematically in 1917 by VRÁNEK [1]), under conditions of experiment very widely differing from ours. This author studied extremely dilute solutions of the salt, with concentrations ranging from 0,01 to 0,0001 mol. per Liter, and experimented always with very small volumes of the solution, — conditions made necessary by the optical method followed by him in this investigation. Nevertheless, the measurements were carried out with much care and a precision as great as possible, yet the results obtained give the impression that the reaction is in reality much more complicated than the author himself seems to believe. For, on the one hand, he thinks it probable with respect to the numbers obtained, that the reaction is a *bimolecular* one, in agreement with the ionic equation suggested above; but his absorption-measurements do not give any numbers, which might be looked upon as true reaction-"constants", and it can be easily seen, that they do not agree really either with a *mono*molecular or with a *bi*molecular process, so that it were better to speak in this case of an accelerated bimolecular, or of a retarded monomolecular reaction. By spectrophotometric observation, he was, moreover, able to demonstrate, that the emeraldgreen solutions have two principal absorption-maxima, for $\lambda = 4260$ A. U., and for $\lambda = 6050$ A. U. respectively; and he stated, that the reaction goes on in darkness as well, light-radiation therefore chiefly acting as an accelerator. The temperature-coefficient of the dark reaction appeared to be rather great (4,56), but that of the photocatalysis, on the contrary, very small; finally an appreciable BECQUEREL-effect through the total volume of liquid is manifested, as soon as it is exposed to the light, which fact could be demonstrated by means of measurements of the electromotive force produced in mixed solutions of *cobalto-* and *cobalti*-salt with respect to a normal *calomel*-electrode, if the solutions are brought from the dark into the neighbourhood of a source of light. VRÁNEK could state as disturbing factors: 1. the slight solubility of the *cobalto-oxalate* formed in the solution of *potassium-oxalate*; 2. the retarding action exerted on the photocatalytic process by the *potassium-oxalate* formed in the reaction, — which influence, however,

[1]) J. VRÁNEK, Zeits. f. Elektrochem., **23**, 336, (1917).

appeared to diminish gradually with increasing concentration of the catalyst; and 3. the tendency of *cobalto-oxalate* to form supersaturated solutions [1]), instead of precipitating normally. Finally there is again a disturbing effect, because of the subsequent photochemical decomposition of the *oxalate*-ion and its transformation into a *formate*-ion, which reaction, as BERTHELOT and GAUDECHON [2]) had already demonstrated formerly, occurs chiefly under the influence of rays of *small* wave-lengths. All the different effects mentioned manifest their special influence in a more or less sensible degree, and they prove sufficiently, how very complicated indeed the whole mechanism of the process is.

The author could, however, not find a catalysing action by addition of acids, such as hydrochloric or sulphuric, under the conditions of his experiments [3]).

§ **3.** In contrast to those of VRÁNEK, our experiments were executed with much more concentrated solutions of the complex salt, while, after many trials, finally the direct gravimetric determination of the *cobalto-oxalate* generated was adopted as method of analysis; the cobalto-salt was determined as metallic *cobalt*, after reduction in a current of dry hydrogen. Even in the case of very concentrated solutions, the error resulting from the solubility of the precipitate in the solution containing *potassium-oxalate*, appeared to be small enough to neglect it in comparison with the other incertitudes of the experiment: in the most unfavourable circumstances the deviations caused by this factor did not surpass 1,5 %.

The dark green liquid was kept in a vessel of transparent quartz, surrounded by a quartz-mantle of greater diameter; in the space between the cylinders a current of water was continually passed, which was kept at an almost constant temperature by means of a metallic spiral-tube, placed in a thermostat; the temperature varied in our experiments between 21° and 23° C. As source of light a quartz-lamp (HERAEUS) was used, which was placed always at exactly the same distance (140 m.m.), and which sent its rays into the solution not before its current had reached a constant and always identical intensity, and also its radiating power had become constant. All the conditions of the experiments were, for the rest, in all cases as constant as possible; e.g. the volume of the solution was always the same, namely 50 ccm. Because also the

[1]) ST. DEAKIN, M. SCOTT and B. D. STEELE, Zeits. f. phys. Chemie, **69**, 126, (1909).

[2]) D. BERTHELOT and H. GAUDECHON, Compt. rend. de l'Acad. d. Sc., Paris **152**, 162, (1911).

[3]) J. VRÁNEK, loco cit., p. 350.

crystallised complex salt is decomposed very slowly, when preserved in darkness, the preparation used in our first experiments contained a very small quantity of the *cobalto*-salt; so that, after its quantity had been determined accurately, the necessary, and only very small correction of the results made necessary by it, was applied in the first series of measurements. The degree of accuracy of the method of analysis was tested beforehand by experiments with mixed solutions of known composition, and it was found really sufficiently great. The solutions were continually stirred by means of a current of *nitrogen*, regulated at about four bubbles every second; later-on stirring was brought about by a current of *carbon dioxide*, after it was found, that the reaction was not influenced by it in any respect. It is necessary to perform the analysis of the solutions in darkness, and to filter the precipitate as rapidly as possible, to wash it immediately, and to carry out all necessary manipulations in rapid succession. As long as the mother-liquor is adhering to the precipitate, all access of light must be carefully prevented, as well as all considerable increase of temperature.

In a first series of determinations, we thus obtained the following data:

Temperature in °C.:	Time of Exposure in minutes:	Corr. Weight of the Cobalti-Salt in 50 ccm.:	Corr. Weight of metallic Co. found:	Percentage of the Salt decomposed:
22°3	60′	0.7247 Gr.	0.0634 Gr.	73.34 %
22.2	60	0.9709	0.0665	51.41
22.2	60	1.2124	0.0695	48.05
22.5	60	1.4655	0.9694	39.70
21.7	60	1.7021	0.0686	33.78
21.9	60	1.9434	0.0699	30.16

Taking into account the unavoidable uncertainties, which always remain in the study of so highly complicated a reaction as this, and attributing only a moderate value to the small increase which the first four numbers apparently show with respect to each other, — it must be evident from these results, that the quantities of the salt decomposed within identical intervals of time are approximately *in*dependent of the initial concentration, and chiefly determined by the amount of light-energy absorbed during that time. The reaction-order is evidently zero, — a fact which may be used as an argument on behalf of the view, that the process is of a purely photocatalytic

character. It might be expected that also a true proportionality would exist between the time of exposure and the amount of decomposed substance, if the initial concentrations were the same in all cases. However, experience only partially confirms this conclusion; at least we found, for instance, the following data in a series of experiments:

Temperature in °C.:	Time of Exposure in minutes:	Corr. Weight of the Cobalti-Salt in 50 ccm.:	Corr. Weight of the metallic Co. found:	Percentage of the Salt decomposed:
23°2	30′	0.0803 Gr.	0.0310 Gr.	26.4 %
23.9	45	0.9017	0.0357	33.2
23.5	60	0.9902	0.0511	44.7

This divergence becomes somewhat intelligible if we remember that the medium is continually changing chemically and physically during the reaction; therefore, because it changes gradually as well in absorptive power as in concentration of the *cobalti*-salt or *potassium-oxalate*, the action of the light in 60 minutes e.g., can *not* be equivalent to twice the action in 30 minutes, etc. On the contrary, there is rather a cause for astonishment at the fact that the results of the first series of experiments were really so regular, while the initial concentrations in these experiments differed so appreciably from each other, and thus the same was true for the absorptive power of the solutions used. It may be, that the slight increase of the first four numbers mentioned above, finds its explanation also in this particular circumstance.

§ 4. Afterwards the experiments described above were again repeated, and now a specially purified salt, free from all *cobalto-oxalate* was made use off. It was freshly prepared and immediately used in the experiments, in which a lamp of somewhat smaller intensity was applied as source of light. For the numbers obtained, see the table on the following page.

From these measurements it appears that the speed of reaction is relatively greater with the smaller, than it is with the greater concentrations; that also in the most favourable circumstances disturbing influences seem to play a rôle, which have as a consequence some uncertainties of the analysis; and that, at least with respect to the last four numbers, the total decomposition may be supposed as *in*dependent of the original concentration. It must be remarked, that

Temperature in °C.:	Time of Exposure in minutes:	Weight of the Cobalti-Salt in 50 ccm :	Weight of metallic Co. found:	Percentage of the Salt decomposed:
22° ± 1°	60′	0.750	0.0567	62.2 %
id.	60	1.000	0.0546	45.8
id.	60	1.250	0.0411	27.5
id.	60	1.500	0.0475	26.5
id.	60	1.750	0.0429	20.5
id.	60	2.000	0.0465	19.5

the mean decomposition in 60 minutes (ca. 0,0445 Gr. *Co*) is here only about $^2/_3$ of that formerly observed, — which may be chiefly caused by the fact, that the intensity of radiation of the *quartz*-lamp was a smaller one than formerly, and by a somewhat modified form of the vessels employed. All these measurements have, therefore, not an absolute, but merely a *relative* significance.

§ 5. Results mutually agreeing much better, however, were obtained in the study of the influence, which the addition of certain electrolytes to the solution has upon the photocatalysis under consideration. For it had soon become evident by preliminary experiments, that, — in contrast to VRÁNEK's negative results of the addition of acids, — a remarkably strong influence on the speed of reaction could be observed, if neutral salts were added to the concentrated solutions of the *cobalti*-salt used by us. An addition of *alcohol* had, however, no appreciable effect; but solutions of neutral salts, if added to the photosensitive solution, have immediately a very distinct influence, when the salts of strong bases and acids are used for this purpose.

Such a catalytic influence of salt-solutions on photochemical reactions has, indeed, been found already by some other authors, e.g. by JORISSEN and REICHER [1]) in the case of the photochemical oxydation of solutions of *oxalic acid* by free oxygen, and by ROLOFF [2]) in the case of EDER's solution: the last mentioned investigator found even one case which seems to be of the same type as those described here.

Subsequently the influence was studied by us, which resulted from the addition of varying quantities of *potassium*, *sodium*, and *lithium chlorides*; in a second series of determinations the analogous influence

[1]) W. P. JORISSEN and L. TH. REICHER, Zeits. f. phys. Chemie, **31**, 142, (1899).
[2]) M. ROLOFF, Zeits. f. phys. Chemie, **13**, 327, (1894).

of *magnesium*, *beryllium*, and *ferric chlorides* was investigated. The choice of such salts is limited by the condition, that only salts of such cations can be used, whose *oxalates* are easily soluble. For in the case of only slight solubility of those oxalates, a part of the cation added would gradually be removed from the solution by precipitation with the *potassium oxalate* set free during the reaction. However, these investigations may be extended eventually by the use of *ammonium*, *rubidium*, and *caesium* salts, while, on the other hand, a wide variation of all kinds of anions will be possible here.

In all experiments the same volume of solution (50 ccm) was used, containing 0,0607 grammol. of the (anhydrous) complex salt per Liter. Moreover, the whole experimental arrangement was in all cases accurately the same, while the time of exposure was always

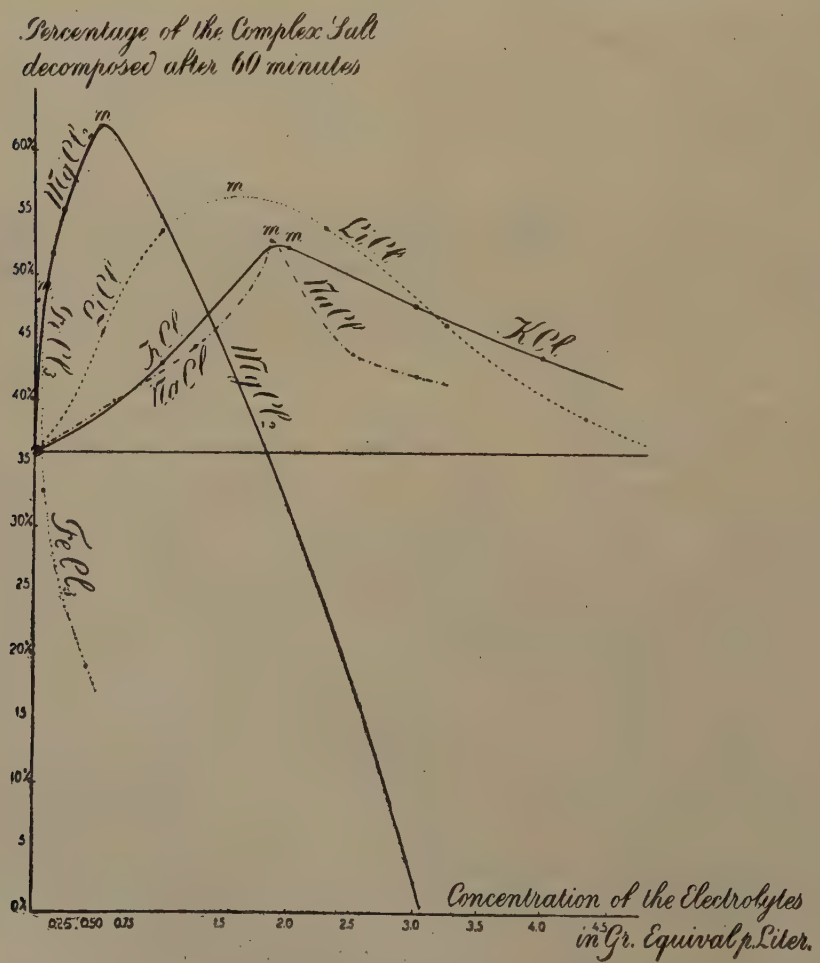


Fig. 1.

I. 50 ccm. of a 0,0607 mol. solution of $K_3\{Co(C_2O_4)_3\}$; KCl as catalyst; time of exposure = 60 minutes; temperature = 21° ± 1° C.

Weight of KCl in Grams in 50 ccm.:	Concentration of KCl in Equiv. per Liter:	Weight of Co found:	Weight of Salt decomposed in Gr.:	Percentage of Salt decomposed:
0	0	0.0648 Gr.	0.4833 Gr.	36.17 %
1.864	0.50	0.0696	0.5196	38.89
3.728	1.00	0.0771	0.5756	43.08
7.456	2.00	0.0935	0.6981	52.24
11.184	3.00	0.0856	0.6391	47.83
14.912	4.00	0.0781	0.5832	43.64
II. Conditions the same as before; NaCl as catalyst:				
0	0	0.0648	0.4833	36.17 %
1.829	0.626	0.0715	0.5338	39.95
3.658	1.252	0.0792	0.5913	44.25
5.487	1.878	0.0946	0.7063	52.85
7.316	2.504	0.0783	0.5846	43.75
9.145	3.128	0.0752	0.5614	42.02
III. Conditions the same as before; LiCl as catalyst.				
0	0	0.0648	0.4833	36.17 %
1.153	0.543	0.0816	0.6092	45.59
2.306	1.086	0.0962	0.7182	53.75
6.918	3.258	0.0827	0.6174	46.21
9.224	4.344	0.0685	0.5114	38.27
11.530		0.0609	0.4547	34.03
IV. Conditions the same as before; $MgCl_2$ as catalyst.				
0	0	0.0648	0.4833	36.17 %
0.299	0.125	0.0930	0.6943	51.96
0.599	0.251	0.0988	0.7376	55.20
1.198	0.503	0.1113	0.8310	62.19
2.396	1.006	0.0983	0.7339	54 92
4.792	2.012	0.0567	0.4233	31.68
7.188	3.018	0.0041	0.0306	2.29

60 minutes. The temperature was 21° ± 1° C.; the concentrations of the solutions of salts used were consecutively varied from 0,1 normal to full saturation. The complex salt used was carefully purified and did not contain any appreciable amount of *cobalto-oxalate*; moreover, the solutions were stirred by the aid of a current of *carbondioxide*, after it had been demonstrated, that this gas had no influence upon the speed of reaction.

Above we have given a review of the results obtained, while in fig. 1 these data are reproduced in graphs, in which the equivalent-concentrations of the electrolytes added are used as abscissae, while the percentages of the original salt transformed, are taken as ordinates in it.

The determinations with $BeCl_2$ and Fe_2Cl_6 are somewhat less accurate, as a consequence of secondary influences, as e.g. the strong hydrolysis of the *berylliums*alt, and perhaps the formation of complex compounds in the case of the *ferric* salt; by these factors the image may be somewhat less definite. The data obtained in these cases follow here :

Weight of $BeCl_2$ in Grams in 50 ccm.:	Concentration of $BeCl_2$ in Equiv. p. Liter:	Weight of Co found:	Weight of Salt decomposed in Gr.:	Percentage of Salt decomposed:
V. Conditions the same as before; $BeCl_2$ as catalyst.				
0	0	0.0648	0.4833	36.17 %
0.009	0,004	0.0383	0.2859	21.40
0.023	0.011	0.0536	0.4002	29.95
0.045	0.023	0.0511	0.3815	28.55
0.090	0.045	0.0404	0.3016	22.57
0.180	0.090	0.0332	0.2479	18.55
VI. Conditions the same as before; Fe_2Cl_6 as catalyst.				
0	0	0.0648	0.4833	36.17 %
0.035	0.013	0.0614	0.4584	34.31
0.087	0.032	0.0798	0,5958	44.59
0.119	0.045	0.0859	0.6413	48.10
0.174	0.065	0.0585	0.4368	32.69
1.044	0.390	0,0348	0.2576	19.28

§ **6**. In these series of observations evidently we cannot speak of real reaction-*constants*: the data available do agree neither with the supposition of a monomolecular, nor of a bimolecular reaction-form.

But all curves of Fig. 1 manifest a clear and obvious *analogy* of shape: they rise evidently all to a steeper or flatter *maximum*, and then decline more or less rapidly. The addition of all these electrolytes thus involves an *acceleration* of the photochemical reaction in the case of smaller concentrations of them, *which, however, reaches a maximum at a certain concentration, characteristic of each salt, and which subsequently again diminishes.* In some cases this diminution may even change into a *retardation* of the process [1]) at concentrations, which are not even so very high; and finally in the case of $MgCl_2$, for instance, the reaction may be stopped even completely by it!

Another very remarkable fact is, *that the maxima are situated at smaller concentrations, as the valency of the cation, i.e. its electrostatic charge, is greater*: for the *bi*valent *Mg*-ion this maximum approaches much nearer to the ordinate-axis, than for the *mono*valent ions of the *alkali*-metals, while the maximum of the curve of the *tri*valent *Fe*-ion is situated in the immediate vicinity of the Y-axis. The *nearer* these maxima approach the ordinate-axis, the more *steeply* the curves will appear to decline after passing the maximum. However, not only the electric charges of the ions, but also their *specific* properties appear to play a part in this: thus, for instance, the three maxima of the curves of the *alkali*-metals do *not* coincide, although their charges are the same; but they approach the *Y*-axis the more closely, the smaller is the atomic weight of these elements. The respective concentrations of the solutions of these three electrolytes, at which the maxima are reached, are, if graphically interpolated, — for *LiCl*, *NaCl*, and *KCl* respectively: 1,65 N. equiv., 1,88 N. equiv., and 1,96 N. equiv.; these concentrations may e.g. be considered as approximatively proportional (1 : 1,14 : 1,18) to the logarithms of the ionic velocities at 18° C. of the three kinds of ions, being here about: 1 : 1,06 : 1,17. Of course, we emphasize, that no especial significance should be attributed to such relations as suggested here, because the number of data is yet too small, and their accuracy not sufficiently great. But attention may be drawn to the fact only that the *specific* properties of the ions play also a rôle in this, and

---

[1]) It may be remarked here, that JORISSEN and REICHER (loco cit.), as well as ROLOFF, found instances of *positive* and *negative* photocatalysis under the influence of neutral salts, however, without making a general supposition about the possible shape of the respective curves. In ROLOFF's paper one case is mentioned, which is in full agreement with the data obtained by us, namely, where he used KNO_3 as a catalyst, and found a maximum of its action at a certain concentration.

that the characteristics of the added salts in this photocatalysis are evidently intimately connected with the electric charges of the ions and with their mutual electrostatic actions upon each other.

If the relations found here, should indeed appear to be generally valid after the investigations have been extended over a much greater number of cases of photocatalysis, it would perhaps appear to be possible to give a theoretical explanation of all these peculiarities and more particularly of the occurrence of a maximal catalysis by salts, starting with the views about the nature of strong electrolytes and their abnormal behaviour, as developed in recent times by BJERRUM [1]), GHOSH [2]), NOYES [3]), and others; which views in every case, however, would involve a complete break with the electrolytic dissociation-theory of ARRHENIUS, at present still almost universally adopted.

Perhaps one of us will return to this question again in future, after a more detailed experimental investigation of this kind has been made.

Laboratory for Inorganic and Physical Chemistry of the University.

Groningen, May 1920.

---

[1]) N. BJERRUM, Zeits. f. Elektrochemie, **24**, 321, (1918); Zeits. f. anorg. Chem. **109**, 275, (1919).

[2]) I. C. GHOSH, Journ. Chem. Soc. London, **113**. 449, 627, 707, (1918).

[3]) A. A. NOYES and MC. INNES, Journ. Amer. Chem. Soc. **42**, 239, (1920).

Chemistry. — *"Colloidal Sulphurcompounds of Ruthenium"*. By Prof. F. M. JAEGER and J. H. DE BOER.

(Communicated in the meeting of May 29, 1920).

§ 1. It was for the first time during the process of recovering *ruthenium* from residues, that we observed some phenomena indicating the existence of colloidal *sulphur*-compounds of that metal. The properties of the colloidal solutions thus obtained, appeared to be sufficiently interesting, to study the phenomena more in detail. The results of this investigation are accordingly summarized in the following paper.

If a solution of freshly prepared *ammonium-sulphide* be added to a *hot* solution of some salt of tetravalent *ruthenium* [1]), be it to the *sulphate*: $Ru(SO_4)_2$, or to a complex salt [2]) like: $\left| Ru\begin{matrix}(HO)\\(NO)\end{matrix}(NH_3)_4 \right| Br_2$, a brownish black precipitate of RuS_2 will be formed, which does not manifest any especially remarkable properties. Totally different, however, is the behaviour of these substances with respect to each other, if the experiment is carried out at *lower* temperatures, e. g. at 0° C.: under these circumstances a dark, greenish black precipitate is formed, while a dark green colloidal solution appears at the same time. This solution is very unstable: it rapidly becomes turbid, depositing greenish black flakes of the same kind as the original precipitate. For the green solution is nothing but a colloidal solution of the original precipitate, produced by the addition of ammonium-sulphide; it shows the TYNDALL-effect, and its dispersed particles appear to carry a *negative* electric charge, as follows from the electric cataphoresis of the solution. On being put into contact with the air for some hours, the solution is completely flocculated, and the supernatant liquid then shows only the yellow colour of the ammonium-polysulphides. The green solution is much more stable, if first strongly diluted with water; but even in these circumstances it appears to be flocculated completely after twenty-four hours. Neither an addition of gum arabic, nor that of gelatine, can increase the stability of the colloidal solution.

---

[1]) U. ANTONY and A. LUCHESSI, Gazz. Chim. It. **28**, (II), 139, (1898).

[2]) A. WERNER, Ber. d.d. chem. Ges., **40**, 2621, (1907).

§ 2. If now the flocculated solution is quietly left standing during a couple of days, its colour becomes gradually pale pink; and after standing somewhat longer, finally a more or less intense reddish violet solution is obtained, while at the bottom of the vessel a precipitate of finely divided sulphur has accumulated. An analogous phenomenon is observed, when one tries to subject the original, dark green solution to dialysis: also in that case a pink solution is finally obtained after the flocculation of the original green one. This new red solution, into which the original green liquid is transformed, also appears to be a colloidal solution: both the original and the red liquid exhibit the TYNDALL-effect and on being examined with the ultra-microscope they both show the characteristic structure and the BROWNian motion of true colloidal solutions. The stability of the red solution appears, however, to be much greater than that of the dark green solution mentioned before.

Soon it became evident that for the change of the unstable green solution into the much stabler red solution, the presence of the free oxygen of the air is essential; that, in other words, an *oxydation*-process goes on, in which the greenish black precipitate originally formed is gradually dissolving under continuous absorption of oxygen, while a red colloidal solution is formed by it. This chain of events could be illustrated, leaving no doubt whatever about its truth, by the following series of experiments:

a. Greenish black *ruthenium-sulphide* freshly precipitated at 0° C. was first washed with icy-cold water, and subsequently dried after washing it with absolute alcohol and ether. Immediately it was mixed with water and shaken in a stoppered bottle; a suspension is formed of an originally bluish hue, the upper layer of which is, however, already after one and a half hour converted into a pale pink liquid. After a day the colour turns reddish violet, while the quantity of the precipitate is gradually diminished, the longer the contact of the different substances lasts. Simultaneously a slight precipitate of sulphur is deposited on the bottom of the flask.

b. At 0° C. freshly precipitated greenish black sulphide, treated as described above, was vigorously shaken with water, and a continuous current of pure air sucked through the liquid. Soon the solution turns reddish violet; after some days the original precipitate has completely disappeared, while some finely divided sulphur only remains, which can be easily removed by filtering. This is one of the best modes of preparing the red colloidal solutions.

c. On being exposed to the air for a long time, the dry greenish-

black sulphide gradually changes its colour, being converted into a reddish, dark coloured mass, which gives immediately the red solution, if shaken with water.

d. A piece of filter-paper soaked in the green colloidal solution, becomes very rapidly violet on being exposed to the air. If the oxygen of the air is first removed, *no* change of colour appears; the precipitate generated in flocculating the green solution gives, however, automatically the reddish violet liquid, when exposed to the atmosphere.

e. Whilst RuS_2, precipitated from hot solutions is simply attacked by nitric acid (spec. grav.: 1,4) and oxydized to a brown solution, the greenish black sulphide is attacked by the same acid extremely vigorously, almost explosively: a red violet solution is formed, while, moreover, some sulphur is precipitated at the same time. The red-violet solution is, also after neutralisation of the acid in excess, slowly oxydized further, when in contact with the air; finally the solution becomes completely colourless, and the slightly acid liquid thus obtained appears to contain a *sulphate*. Not even a preliminary dilution of the red-violet liquid with water can prevent this oxydation to sulphate. The presence of mere traces of the unstable greenish black sulphide may be proved by this reaction of oxydizing the supernatant liquid by means of nitric acid [1]); and it is in this way, that we can demonstrate the fact, that the sulphides precipitated from *ruthenium* solutions by ammonium sulphide between 0° C. and boiling-temperature, are really mixtures of stable RuS_2 and the unstable greenish black sulphide, here described. It suffices to shake the precipitate simply with water, and to add strong nitric acid to this suspension: the red colour will then appear immediately.

§ 3. Because the new sulphide appeared to lose its characteristic properties, if heated even to only 110° C., it was necessary, under exclusion of the oxygen of the air as much as possible, to prepare it always at *lower* temperatures; also it must be rigorously purified for the purpose of analysis. In the process of precipitation, free sulphur is moreover always formed, — a fact also noticeable [2]) in working with other ruthenium sulphides, — and therefore necessitating repeated

[1]) Already other investigators have occasionally had an opportunity to observe a pink coloration of the solutions obtained in their studies on *ruthenium sulphides*, without any attempt at an explanation of the said phenomenon, it was e.g. mentioned by ANTONY and A. LUCHESSI, loco cit **30**, (II), 540, (1900).

[2]) C. CLAUS, Ann. der Chem. u. Pharm., **59**, 245, (1846); U. ANTONY and A. LUCHESSI, Gazz. Chim. Ital. **30**, (II), 539, (1900).

extraction of the product by carbon disulphide at low temperatures. The substance was, therefore, rapidly put into a small ERLENMEYER-flask, carbon bisulphide was poured upon it, the air driven out by carbon dioxide, and the flask shaken for some time at room-temperature. This treatment was repeated several times, till no sulphur was any more extracted; the carbon bisulphide was then washed out by a mixture of dry alcohol and ether, the product finally washed with absolute ether and carefully dried in an atmosphere of carbon dioxide. For the purpose of analysis a weighed quantity was put into a ROSE-crucible, which in its turn was hung inside a nickel crucible, and carefully roasted with access of the air; afterwards it was ignited in a current of dry hydrogen. All the determinations were made by means of a micro-balance.

Analysis: 12,33 m.Gr. of the greenish black sulphide gave 4,26 m.Gr. *Ru*; calculated for RuS_6: 34,69 % *Ru*; found: 34,55 % *Ru*.

Because in the oxydation of this sulphide, as will be demonstrated below, there is formed a substance containing four atoms of sulphur, while simultaneously sulphur is set free, this high content of sulphur is perfectly in agreement with the whole chemical behaviour of the greenish black sulphide [1]), which has the character of a *ruthenium persulphide.*

§ 4. We must now first review the properties of the red-violet solution, which is formed by oxydation of the green solution described above. Its refractive index appeared to be practically identical with that of pure water; moreover, besides the TYNDALL-effect and the BROWNian movement, it manifests in a particularly beautiful way the phenomenon of electric cataphoresis: the dispersed particles possess, in contradistinction to those of the green colloidal solution, a *positive* charge. Although the solution is very stable, and may even be concentrated on the water-bath without coagulation, it can be flocculated by the addition of electrolytes, — be it only slowly. The pure solution was mixed with a small quantity of solutions of NH_4Cl, $CaCl_2$, Fe_2Cl_6, K_2SO_4 and Na_2HPO_4. Already after a day some precipitate was formed from each of these liquids, and the intensity of their colour diminished. If more of the electrolytes be added, the precipitate formed first again disappears, but after twenty-four hours a certain quantity is again deposited. After a couple of days the colour of the liquid has completely disappeared, and all of the dispersoid has been flocculated. Most rapidly this takes place, when *phosphate* is added,

[1]) It may be remarked here, moreover, that on heating this sulphide at the open air at 120° C., also SO_2 is formed; the sulphur seems to be partially more loosely bound than the remaining part of it.

the electrostatic charge of the anions, therefore, being decisive here, — a fact, which is in agreement with the stated positive charge of the dispersed particles. Such experiments were also carried out with a more concentrated solution, $CaCl_2$ being added to it. After one day already there appeared a precipitate, the colour of the solution being violet; after two days more precipitate was formed, while the colour became bluish violet; after five days the colour was dark bluish violet; after a fortnight it was similar and only a relatively small amount of precipitate was formed. In no case the colloidal solution was flocculated completely, it, therefore, appearing to be extremely stable. This follows also from the behaviour of the liquid, while being concentrated on the waterbath: even the last drops retain their bluish violet colour, and the amorphous reddish violet powder, which is continually deposited at the surface-border of the liquid, may be redissolved immediately into a colloidal solution of the same kind as the original liquid. This reversibility of the colloid corresponds also here with a smaller sensitiveness to electrolytes. On complete evaporation a violet and a grey powder are obtained; only the violet one is reversible. If heated for some time, it turns grey, afterwards black, and then it can no longer be dissolved. After being dried at 110° C. until the weight has become constant, the powder is black and possesses a metallic lustre.

Of this product the content of *ruthenium* was determined in the way formerly described, and by the aid of the micro-balance.

Analysis: 17,23 mGr. of the powder contain 4,55 mGr. *Ru*. The amount of sulphur was determined by volumetric analysis: a solution, the *ruthenium*content of which was accurately known, was oxydized by a solution of potassium-permanganate of known strength, and the amount of sulphate afterwards estimated as $BaSO_4$. Such solutions were prepared from a known weight of the pure greenish black sulphide by oxydation of its solution by means of an air current.

Analysis: A quantity of the solution containing 2,40 mGr. *ruthenium*, gave 21,4 mGr. $BaSO_4$, corresponding with 2,93 mGr. *sulphur*, this being 32,18 %. Therefore 41,42 % of *oxygen* is present, corresponding with the formula: RuS_4O_{10}, which was afterwards confirmed by other tests.

Calculated for RuS_4O_{10}:	*Observed*:
Ru: 26,16 %	26,40 %
S: 32,82 %	32,18
O: 41,02 %	41,42 %

The oxydation of the solution to *ruthenium sulphate* and free *sulphuric acid* can, therefore, be expressed by the equation:

$$RuS_4O_{10} + 4O = Ru(SO_4)_2 + 2SO_2,$$

which was completely checked and confirmed by the determination of the oxygen liberated from the permanganate used and absorbed by the substance, as well as by the quantitative measurement of the amount of sulphuric acid formed. For this latter quantity is equal to the total amount of acid found, minus the acid added for the volumetric analysis, plus the quantity of acid used during the titration with $KMnO_4$.

Analysis: A quantity of the colloidal solution, containing 2,30 mGr. of *ruthenium* (= 0,0225 milli-mol. *Ru*) was titrated with 10 ccm. of a $\frac{1}{25}$ normal solution of sulphuric acid and 4,9 ccm. $KMnO_4$ of 0,09 normal, — if a normal solution be calculated as one containing 0,4 mol p. Liter, equivalent to 0,09 mGr. atom *O* p. ccm. Therefore, totally 0,0882 mGr. *O*, corresponding with 4*O* to 1 *Ru* were used. As there are used at the same time 2,65 ccm. H_2SO_4 of the strength mentioned above in this reaction, 7,35 ccm. sulphuric acid remain. As 38 ccm. of $\frac{1}{100}$ normal $NaOH$-solution were necessary in the subsequent titration, and for 7,35 ccm. H_2SO_4 only 29,4 of this $NaOH$-solution were necessary, it follows that 0,043 milli-mol. H_2SO_4 are formed in the reaction by oxydation of the sulphur. For every atom *Ru* there are thus formed 2 molecules H_2SO_4, which data, with respect to the quantity of *O* absorbed in the process, demonstrate clearly the correctness of the equation just mentioned.

§ 5. Thus, while the original greenish black sulphide appeared to be RuS_6, this is transformed by vigorous absorption of atmospheric oxygen into the reddish violet compound RuS_4O_{10}, with simultaneous splitting-off of free sulphur, according to the equation:

$$RuS_6 + 5O_2 = RuS_4O_{10} + 2S,$$

while the compound formed is afterwards further oxydized by the potassium permanganate according to the equation:

$$RuS_4O_{10} + 4O = Ru(SO_4)_2 + 2H_2O_4.$$

The red colloid is, therefore, by no means to be considered as the final oxydation-product of the greenish black sulphide, but it represents an intermediate stage on the way leading finally to *ruthenium sulphate*. This fact too could be confirmed by special reactions:

a. Strong nitric acid oxydizes the red coloured solution at low temperatures slowly, but on heating more rapidly, to a solution which appears to contain free sulphuric acid.

b. A solution of potassium permanganate makes the colour of the

colloidal solution and that of the permanganate rapidly disappear, while in the liquid SO_4-ion becomes demonstrable.

c. Addition of H_2O_2 and some diluted acid soon makes the colour of the solution disappear, while sulphate is formed.

d. The red-violet powder obtained by evaporation from the solution, prepared by oxydation of the original green solution by the air, no longer gives a reddish violet colloidal solution, after being exposed to the air for three weeks; it gives a slightly greenish solution of acid reaction, containing a perceptible amount of SO_4-ion.

These different reactions prove undoubtedly, that the violet RuS_4O_{10} is an intermediate product, which by further absorption of oxygen is transformed into the sulphate: $Ru(SO_4)_2$. The compound has the composition of a normal *ruthenium*salt of*pyrosulphurous acid : $H_2S_2O_5$*, and more particularly, of a *pyrosulphite* of *tetra*valent *ruthenium.* In this way the *pyrosulphite* appears as an intermediate product in the oxydation-process of *ruthenium-persulphide* to *ruthenium-sulphate;* most remarkable in it is, moreover, the colloidal nature of this intermediary *ruthenium-pyrosulphite,* the dispersed particles of which bear at the same time an electrostatic charge of opposite algebraic sign to those in the colloidal solution of the original *persulphide.*

Some other reactions of the colloidal *pyrosulphite* may be of interest here:

a. The colloidal solution of the salt is rapidly decolourized by strong *sulphuric acid.*

b. Hydrochloric acid, especially in higher concentrations and at higher temperatures, has the same effect, while sulphuric acid is formed simultaneously.

c. Sodium hydroxide (1 : 3) slowly decolourized the solution, but at higher temperatures even a more dilute solution does this rapidly.

d. On addition of *mercurous nitrate,* the violet colour disappears immediately; a brown turbidity appears, and, after some hours, a brownish black precipitate is formed, which is probably a sulphide of mercury.

e. Ammonium sulphide does not give a precipitate, but makes the colour disappear; *sulphurdioxide,* however, has no appreciable effect.

f. A solution of *silver nitrate* turns the colour slowly into a brown one, and a brownish black precipitate is gradually formed, which is soluble in ammonia.

g. On boiling the colloidal solution with *sodium carbonate,* the colour is rapidly changed into a pale green one.

h. A concentrated violet solution turns blue on addition of a dilute acid; but after neutralizing with a base, the red-violet colour is restored; etc.

SUMMARY.

In the above we were able to demonstrate, that the product of the precipitation of a salt of tetravalent *ruthenium* by *ammonium sulphide* differs with the temperature: at 100° C., brownish black RuS_2 is formed besides free sulphur, but at 0° C. greenish black RuS_6 is formed, which has the character of an irreversible colloidal substance, and which in the presence of ammonium sulphide in excess, gives a beautiful green, but unstable colloidal solution. At intermediate temperatures mixtures of both sulphides are formed besides free sulphur.

The dark green sulphide and the green colloidal solution of RuS_6, the particles of which are negatively charged, rapidly absorbs free oxygen, and is transformed into a reddish violet solution of the reversible colloidal *ruthenium-pyrosulphite*: RuS_4O_{10}, the particles of which bear a positive electrostatic charge. This salt is, in its turn, changed by oxygen (air, nitric acid, permanganate) into *ruthenium sulphate* and free *sulphuric acid.* The properties and reactions of these different products were investigated on general lines.

Laboratory for Inorganic and Physical Chemistry of the University.

Groningen, May 1920.

Anatomy. — *"On the Index cephalicus and the absolute Dimensions of the Head of the Population of Holland"* By Prof. L. Bolk.

(Communicated at the meeting of March 27, 1920).

For a general anthropological characterization of a people or a race, one is generally restricted to the three following characteristics: the degree of pigmentation, the length of the body and the proportion of the greatest length of the head or skull to the greatest breadth, expressed in a proportionate number, the so-called Index cephalicus.

This is calculated according to the formula $\frac{100 \text{ breadth}}{\text{length}}$, and as the length always surpasses the breadth, the Index cephalicus will always be expressed by a number smaller than 100. When the Index cephalicus rises above 80, the head is called brachycephalic; when it falls below 75, the term dolichocephalic is applied to it. Indices between 75 and 80 are characterized as mesocephalic. The Index cephalicus — being a proportionate number — does not teach us anything about the real dimensions of the head or skull, every value of the Index may occur with larger and smaller skulls and heads.

Some time ago I communicated the result of very extensive investigations on the two first mentioned anthropological characteristics — the degree of pigmentation and the length of the body, so that I may assume a sufficient knowledge of this physical disposition of our population. Until now this was not the case with the third characteristic — the Index cephalicus — because it is not so easy to obtain data for this in sufficient number, as for the characteristics mentioned before. It is true that I previously communicated data [1]) on the Index cephalicus, but these were based ona comparatively small number of measurements and so they must be considered as provisional communications only.

I have gradually gathered a number of data, in my opinion sufficient, to te able to construct a reliable image of the Index cephalicus

[1]) De Bevolking van Nederland in hare anthropologische samenstelling, in "Gallée, Het Boerenhuis in Nederland en zijn Bewoners", Utrecht 1909.

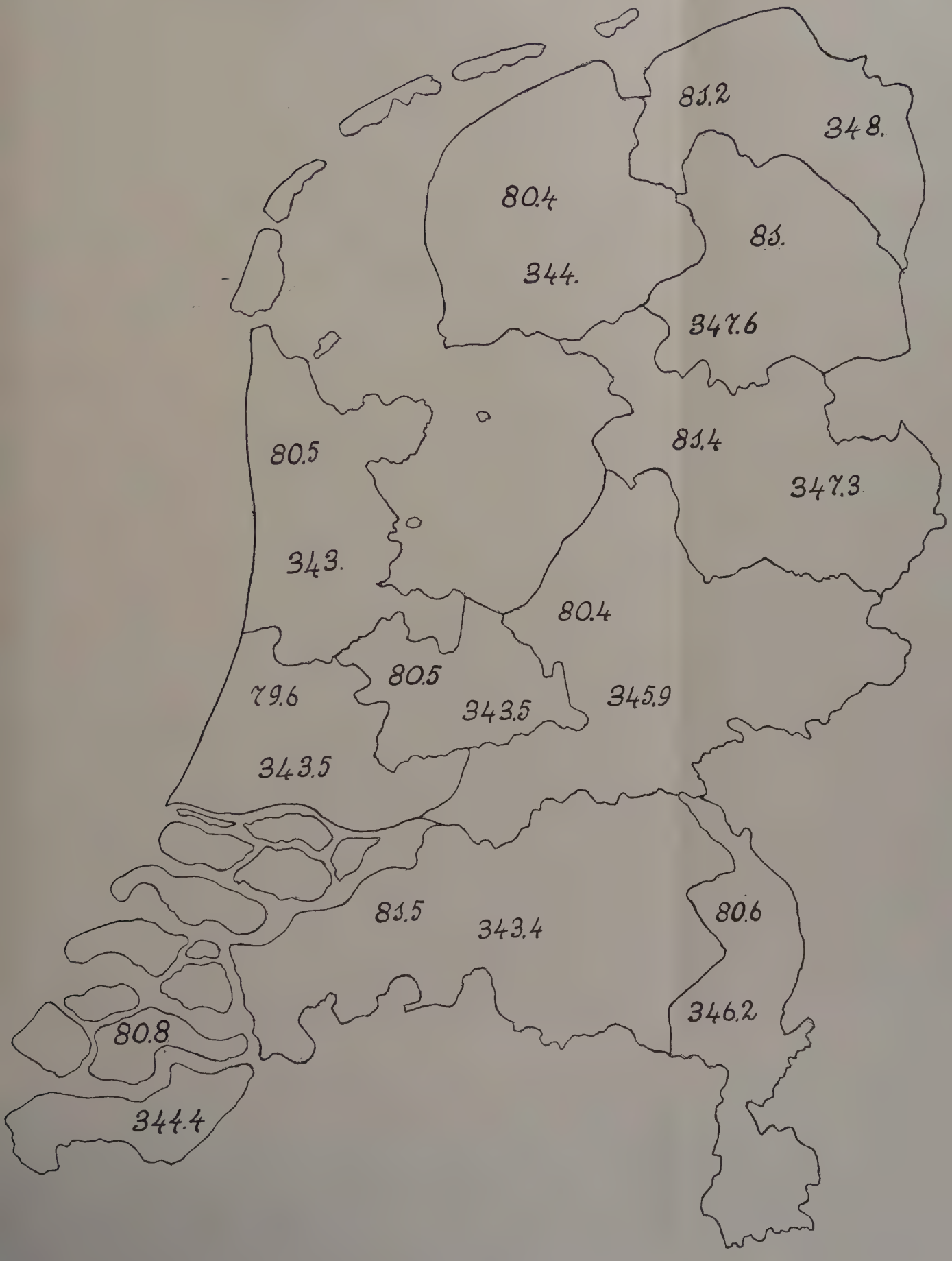
of the Dutch population, taken as a whole. To obtain this, it was of course necessary to gather the measurements of the heads of a sufficient number of people out of every province, and besides, from as many as possible different parts of the province. The result of my investigations is, that the data of 9975 male inhabitants of Holland are at my disposal, which are divided according to the provinces as follows:

Groningen 290, Friesland 768, Drente 460, Overijsel 467, Noord-Holland 1326, Zuid-Holland 1495, Gelderland 1379, Utrecht 430, Zeeland 1243, Noord-Brabant 883, Limburg 1243. These numbers, though rather different, may be considered sufficient for the stating of the provincial averages.

In the anthropological literature one is used, with reference to the head, to restrict oneself to communicating the average value of the Index cephalicus of some group of population and the statistic of the different values from which the average of the index is derived.

But, as I said before, the Index cephalicus is a proportionate number, and so it does not teach us anything about the absolute measurements of the head or skull. Yet I think that the absolute dimensions of the head, from an anthropological point of view deserve more notice than they do now, because they give, after all, an idea of the size of the head, as is the case with the length of the body. In fixing the sum of the average length and breadth of the head of a certain group of the population, one has a datum, which though insufficient, is approximately a standard for the size of the head. And this standard is even more reliable than the contour of the head, as, by fixing the latter, the varying thickness of the hair is included individually. My opinion is, that the sum of the breadth and the length of the heads is a rather reliable datum, to answer the question by comparison, whether the heads of the inhabitants of the different provinces are about the same size, or whether they differ in this respect. I worked out my data in this direction and here I give the result of my investigations.

These results are given on the map, added to this article. Two numbers are placed in every province. The number placed in the northern part of the province teaches us the average Index cephalicus of the persons measured; the southern cipher denotes the sum of the average absolute length and breadth of the heads of these persons. So both these numbers are provincial averages. This does not apply however to the numbers in the provinces of Noord- and Zuid-Holland. The numbers mentioned here only refer to the people measured in these provinces, after deduction of those living in


81.2
348.
80.4
344.
83.
347.6
80.5
81.4
347.3
343.
80.4
80.5
79.6
343.5
345.9
343.5
81.5
343.4
80.6
346.2
80.8
344.4

Amsterdam and Rotterdam. The averages of these will be mentioned separately, and this will give an explanation why they were excluded from the calculation of the provincial averages.

Let us consider first the Index cephalicus. The following tables show the value of the Index cephalicus in the different provinces.

Province	Index cephalicus	Number of people measured
Groningen	81.2	290
Drenthe	81.—	460
Overijsel	81.4	467
Friesland	80.4	768
N. Holland	80.5	736
Utrecht	80.5	430
Gelderland	80.4	1379
Z. Holland	79.6	1239
Zeeland	80.8	1243
N. Brabant	81.5	883
Limburg	80.6	1234
Amsterdam	79	590
Rotterdam	79.2	256

In this table are mentioned also the numbers related to Amsterdam and Rotterdam, these data will be referred to later on. From the table mentioned above, it appears that taking the small geographical extension of our country into consideration, the Index cephalicus is rather variable, as it oscillates between the two extremes 79.6 (Z. Holland) and 81.5 (N. Brabant).

On comparing the provincial averages with each other, one cannot help noticing a certain regularity in the variability. The three northern provinces: Groningen, Drenthe and Overijsel form more or less one group, in which the Index cephalicus attains the value of 81 or surpasses it even.

One might add to this north-eastern territory the so-called Achterhoek of Gelderland of which 313 persons are measured with an average Index cephalicus of 81.1. This north-eastern part of our population forms, as is generally known, linguistically and ethnolo-

gically a more homogeneous part, it is the Saxon element of our population, which distinguishes itself by a higher Index cephalicus.

A second group includes the provinces of Friesland, N.-Holland, Utrecht, Gelderland and Z.-Holland, in which the Index cephalicus is strikingly equivalent, with the exception of Zuid-Holland, in which a relatively strong decline occurs. The average would be lower for Gelderland too, if the population of the "Achterhoek" — with its own Index of 81.1 — had been left out of consideration.

In the second group the Index cephalicus reaches its highest point in 80.5; consequently the population of these provinces is a little more long-headed than that of the north-eastern part of our country. This is most evident in the province of Zuid-Holland, in which the inhabitants have the smallest degree of round-headedness.

The part of our country meant here, is that one, in which the Frisian element of our population predominates and which is characteristically different from the Saxon element by a larger degree of long-headedness.

The three southern provinces, which, according to my investigations, as regards the pigmentation of the population, form a unity, are not uniform as regards the Index cephalicus. The index reaches its highest point, viz. 81.5 in N.-Brabant, from which it appears, that here the most round-headed part of our population lives. Limburg and Zeeland agree, with only a slight difference, and are nearer to the proportion, occurring in the Western provinces. In connection with the high degree of pigmentation these facts point to the population being very mixed. However, this is easy to point out for the province of Zeeland. While the Index cephalicus amounts to 80.08 for the whole of the province, it falls to 79.9 with respect to Walcheren. The population of the most western part of Zeeland has a more long-headed type than the people living in the eastern part. This phenomenon is not unique. In the provinces of Noord- and Zuid-Holland the people, living in the villages on the coast and on the edge of the dunes have a longer and narrower head than the people living more inland.

About this fact, I said before, that the populations of Amsterdam and Rotterdam were left out of account for the calculation of the Index cephalicus of the provinces of Noord- and Zuid-Holland. I did this on purpose, because the inhabitants of these towns have a lower average index than the population living in the country. And because the number of those citizens measured, does not form an unimportant part of the whole population of the province, the value of the provincial average would be influenced too much by the

town average. That was the reason why I did not take these citizens into consideration, in fixing the provincial average.

The difference between the indices of the population of the two towns and of the province in which these towns are situated, are apparent from the foregoing and from the following table.

Noord-Holland	in the country	80.5
	Amsterdam	79.—
Zuid-Holland	in the country	79.6
	Rotterdam	79.2

A comparison of these indices teaches us that the people of both these big towns have a relatively narrower head than the people living in the country, surrounding these towns. This fact is not new, it has been well-known for a long time that in general the population of a town belongs to a more long-headed type than the people living in the country, this rule holds good also for the towns of Amsterdam and Rotterdam.

As far as I had a sufficient number of data at my disposal, I sought, in how far this rule could be applied to towns of a smaller size. This fact is proved by the following data for the towns of Utrecht, Arnhem and Haarlem.

Utrecht (province)	80.5
Utrecht (town)	79.1
Gelderland	80.4
Arnhem	79.4
N. Holland	80.5
Haarlem	79.4

Adding to these data those, mentioned above for Amsterdam and Rotterdam, it is obvious that in the towns mentioned above, the Index cephalicus oscillates between 79 and 79.4, and this is comparatively far below the provincial averages. The citizen has, as regards the proportions of his head, a type of his own, opposed to the rural people and this type occurs already in towns of a relatively small extent. We only state this fact without going farther into the importance or into the theories, based on this fact.

Let us consider now the second group of numbers, which are marked in the provinces on the map added to this article and which refer to the absolute measurements of the head. The number indicates the sum of the greatest length and greatest breadth of the head.

These numbers are useful to a certain extent to give an approximate answer to the question whether on an average the head of some part of our population is larger or smaller than that of the remaining part.

The results for the different provinces are laid down in the following table. For every province the average greatest length, breadth, and the sum of the two values is expressed in millimeters. The data of Amsterdam and Rotterdam are left out of consideration, because of the fixing of the provincial average, these will be communicated separately.

Province	Length	Breadth	Total
Groningen	192	156	348
Friesland	190.6	153.4	344
Drenthe	192	155.6	347.6
Overijsel	191.4	155.9	347.3
N. Holland	190	153.—	343.—
Z. Holland	191.2	152.3	343.5
Utrecht	190.3	153.2	343.5
Gelderland	191.7	154.2	345.9
Zeeland	190.4	154.—	344.4
N. Brabant	189.2	154.2	343.4
Limburg	191.7	154.5	346.2

On comparing the data in the last row, we are struck first by the fact that the difference between the highest and lowest value is remarkably small. The lowest value was found in Noord-Holland, where the sum of the average length and breadth of the head amounts to 343 mm., while Groningen with 348 mm. is the highest in the series. The largest difference amounts only to 5 mm. This difference is so small that one would feel inclined to consider it unimportant. But a look at the map convinces us that a certain regularity in the differences of the provincial averages cannot be denied. On comparing the data on the map, it is evident, that without any exception, the eastern provinces indicate a higher sum-average than the western provinces. To say it differently: though the increase is small, it is yet unmistakable that in the direction of the eastern frontier of our country the heads are larger as far as this size may be expressed

by the sum of the length and the breadth of the head. This may appear from the following table, in which the eastern and the western-provinces are ranged side by side.

Noord-Holland	343	Groningen	348
Zuid-Holland	343.5	Drenthe	347.6
Utrecht	343.5	Overijsel	347.3
Zeeland	344.4	Limburg	346.2

To the second series might be added the Achterhoek of Gelderland with an average of 346.2.

In my opinion the contrast between the two series is too regular for not having any significance. On looking for any connection with the ethnological elements of our population, it appears that the average is smaller, where the Frisian element is represented, while the Saxon element has a higher average. In this respect the difference between the population of Friesland (344 mm) and Groningen (348 mm.) is very evident.

From the following table it appears that the breadth as well as the length of the head of the eastern population exceeds those of the western population.

Average breadth of the head.

Groningen	192	Friesland	190.6
Drenthe	192	N.-Holland	190.—
Overijsel	191.4	Z.-Holland	191.2
		Utrecht	190.3

Average length of the head.

Groningen	156	Friesland	153.4
Drenthe	155.6	N.-Holland	153.
Overijsel	155.9	Z.-Holland	152.3
		Utrecht	153.2

Though both the dimensions of the north-eastern population are larger, the difference between the breadths is greater than that of the lengths. Consequently the people living in the east of our country have rounder heads and a greater Index cephalicus than those living in the western provinces.

The last question to be answered is: how does the population of the two large towns stand in proportion to the people living in the country, surrounding these towns, with reference to the absolute measurements?

Concerning Amsterdam, the following averages were fixed: Length of the head 191.5, breadth of the head 151.3.

On comparing these numbers with those of the province of N.-

Holland (190 resp. 153) it appears that the population of Amsterdam has longer and narrower heads than the rural population.

This is the cause of the Index cephalicus of the population of the town being so much lower (79) than the Index cephalicus of the rural people (80.5).

In Rotterdam I found the following averages: Length 190, breadth 150.5. On comparing these measurements with those of the country, it appears that both breadth and length are smaller.

The same peculiarity may be applied to the people living in the towns of Utrecht and Arnhem, as is evident from the following data:

Utrecht	Length	Breadth
Province	190.3	153.2
town of Utrecht	190	150.6
Gelderland		
Province	191.7	154.2
Arnhem	190.—	151.5

As regards the towns of Rotterdam, Utrecht and Arnhem, the head is shorter and narrower, in fact smaller, than that of the people living in the country, surrounding these towns. As the differences between the breadth-dimensions are larger than those between the length-dimensions, the Index cephalicus of the inhabitants of the town is smaller than the Index cephalicus of the rural people.

Physiology. — *"Experimental proof for the active dilatation of cross-striated muscle-tissue"*. By J. BRAMSON. (Communicated by Prof. G. van RIJNBERK). (After experiments made in the Physiological Laboratory of the University of Amsterdam).

(Communicated at the meeting of January 31, 1920).

We are accustomed to observe that a muscle, after contraction, regains its original length by mechanical influences from without. So in situ, by contraction or tonus of antagonists, and outside the body by gravitation, eventually by weights, stretching the muscle.

In 1871 LUCIANI [1]) discussed the question whether dilatation of a muscle was an active process. He wanted to explain the diastole of the heart partly by the active dilatation of the myocard.

We need not be surprised in the least that tissue dilates actively, when we only think of the formation of pseudopodies in the case of amoebes and leucocytes.

But it was not thought possible however that *cross-striated* muscle tissue could regain its original length by its own force, because a muscle, put on mercury, does not lengthen again after contraction.

In 1900 KAISER [2]) pointed out that the frog's sartorius lengthens again actively on mercury, when oiled. He thought he had proved the active dilatation by this.

To this however an objection was raised, not without reason, that every particle of the muscle, owing to gravitation tries to place itself as low as possible and yields to this impulse, as soon as the contraction of the muscle ceases. It expands on the mercury as much as possible and thus it becomes longer again.

Consequently the problem acquired a different aspect. The muscle had to lengthen itself, while it was withdrawn from the gravitation. This is possible by bringing it into a liquid of the same specific weight as the muscle has, viz. of 1,041.

The difficulties, connected with this, are very great. A salt- or sugar-solution of specific weight is not isotonic. Even a raffinose

---

[1]) L. LUCIANI. Dell' attività della diastole cardiaca. Rivista clinica Bologna.

[2]) K. KAISER. Ueber die Wiederausdehnung des kontrahirten Muskels. Centralbl. für Phys. XIV p. 195.

solution of this specific weight still causes a depression of the freezing-point $\Delta = -0{,}59°$ C. Ureum penetrates quickly into the muscle and makes it soon heavier. Most of the other organic compounds, which are heavier than water are little soluble, have strong viscosity (albumen), are more or less poisonous, irritating or anaesthetic.

I used a mixture of chloroform and benzene of a specific weight of 1,041, in which the muscle could be suspended, and I noticed several times very distinctly that the muscle lengthened itself again after the contraction. As chloroform and benzene are both very strong poisons, one is able to observe the muscle only for several minutes in this medium.

I think I may ascribe the fact that these poisons do not affect the muscle immediately, to a capillary layer of Ringer's that wets the muscle and through which both the liquids diffuse only slowly.

Attempts to take a photograph of this phenomenon have not yielded beautiful results, owing to little secondary movements of the muscle (streams in the liquid through the contraction-push etc.). A cinematographic photo would give better results in this respect.

Looking out for a better recording method, I thought I might be able to apply the graphic method, generally used in the muscle physiology, though this seemed very doubtful, taking into consideration the extremely inconsiderable energy of the dilatation.

Yet by using an instrument of a minimal mass and friction I succeeded in recording a curve (Fig. 1). One sees on this figure a fragment of a curve. The upper row are curves of simple muscle shocks in Ringer's liquid, the two following rows are curves of tetani in the same liquid. The 4th row is a curve of tetani in a mixture of chloroform and benzene. The five lower rows are simple shocks in this mixture. All the curves are of the same muscle. The steep part of the curve is the contraction, the dilatation is very clearly perceptible, but much slower.

A considerable improvement has been made in this method of registration by Professor VAN RIJNBERK, who suggested to me the principle of a very useful instrument. It consists of a glass tube, with a hole in the side, over which an extremely thin membrane of rubber is stretched. A needle is stuck through it, which writes with one end on a sooted drum, placed horizontally and with the other end is stuck in the Achilles tendon of the frog's gastrocnemius. The other end of the muscle is attached to a hook, which serves at the same time for one stimulus-electrode. It pierces a cork, which shuts off the tube on one side. Each of these stopcorks is perforated

by a glasstube through which the apparatus can be quickly filled with a liquid (Fig. 2).

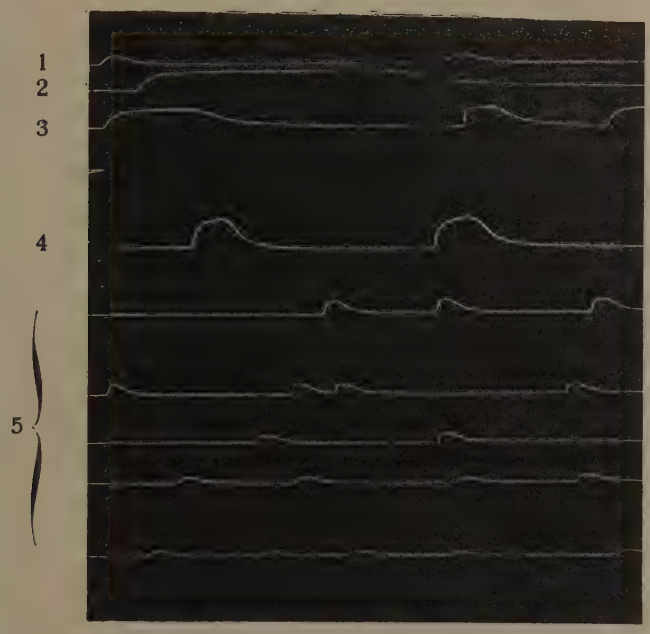


Fig. 1. Myograms of a suspended frog's gastrocnemius (real size).

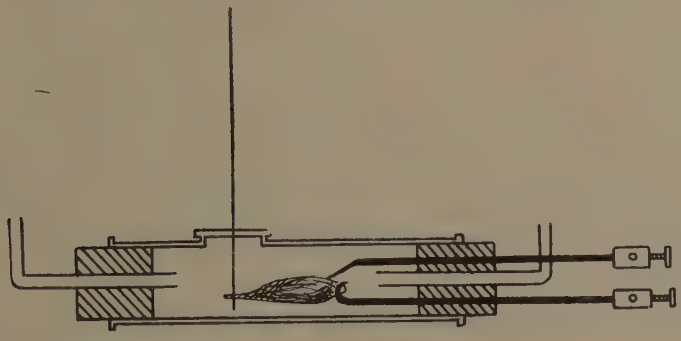


Fig. 2. Apparatus used for the recording of the reproduced myograms in fig. 1 ($^1/_2$ of the real size).

From the preceding communication we may conclude that the dilatation occurs with so much force that it is able to overcome the friction of the writing-needle over the drum.

I put the question to myself whether the muscle would be able to *lengthen itself in opposition to the gravitation*. This led me on to two new proofs:

When we do not put the muscle into chloroform and benzene,

but into a Ringer's solution, then it will bulge between the two points A and B on which it is hung, the apparatus being held horizontally. It is easy to understand that the gravitation brings the two points A and B closer to each other, but can never make them diverge. Consequently the gravitation will act against the dilatation. Notwithstanding this the muscle lengthens itself again. Owing to this observation we are able to record curves without the stretching weights, which always deform the curve, while we need not use the poisonous chloroform-benzene mixture.

When it was once stated that a muscle is able to lengthen itself in opposition to the gravitation, I tried if it would even be able to raise its own weight. I succeeded actually in seeing a muscle, placed vertically, fastened at the lower end, lengthen itself after contraction. This fact had been observed some days before, but without my knowledge, by Dr. BAKELS and Mr. PRAKKEN, in this Laboratory.

It being proved that cross-striated muscle tissue dilates actively, two new points of view have been opened:

1. We are able to record curves, excluding all the forces which could deform it.

2. With the aid of this technique it will probably be possible to find a solution to the problem, raised by the result of my experiments. The question is: what intramuscular forces cause this dilatation and through which are they influenced? The dilatation may be caused by the perimysium externum, the sarcolemma, the sarcoplasma or by the fibrils.

I can state at all events, that the perimysium externum is not able to cause the dilatation only by itself (by its elasticity), for even a fragment of muscle tissue, cut out by me, actually lengthened itself again. The sarcolemma, which is a homogeneous elastine-membrane, has a tendency to diminish its surface, in other words: to take the globular shape.

Consequently it will never be able to lengthen the muscle.

December 19th 1919.

Physiology. — *"Identity of the blood-digestive and gelatine-liquefying bacterial actions."* By Prof. J. J. VAN LOGHEM. (Communicated by Prof. C. EYKMAN.)

(Communicated at the meeting of March 27, 1920).

In investigations on the determination of the so-called specific El-Torvibrios with regard to choleravibrios, I obtained as a result of more general importance a sharper definition of the idea "haemolysis" [1]). By admitting that the changes in the blood, caused by bacteria, may be of different nature, I suggested to understand by *haemolysis* only the causing of *oxyhaemoglobin to come out* from the red blood corpuscles; I opposed to this the *digestion* of blood elements by bacteria, which I indicated as *haemo-digestion.*

Investigations by others (GRIEG [2]) LÖWY [3]) FLU [4]), KRAUS [5]), SOPHIE WOLLMANN [6]) have taught us the practical significance of these for the distinction of choleravibrios. BAERTHLEIN [7]) pointed out the necessity of a right distinction of these ideas, also in the case of other bacteria, whereas SNAPPER [8]) — in connection with his investigations on the decomposition of oxyhaemoglobin in the alimentary canal — has occupied himself with the nature of the digestion.

The following illustrates the latter problem.

Some time ago already, I put the question whether the haemodigestive quality of the choleravibrio is identical with its collolytic capacity and I mentioned several facts which pointed to this possibility.

1. Both the qualities are transient and their decline runs parallel in a certain strain.

2. The processes of the haemodigestion and of the gelatine-lique-

---

1) Centralbl. f. Bakt. Ie Abt. Orig., vol. 57, 1911; vol. 67, 1913 and vol. 70, 1913; Ned. Tijdschr. v. Geneeskunde, 1915, II, p. 22.

2) Indian Journal of medical research, vol. 2, 1914.

3) Centralblatt f. Bakt., I, Orig., vol. 75, 1915.

4) Geneeskundig Tijdschr. v. Nederlandsch Indië, vol. 53, 1913.

5) Die Cholera asiatica und die Cholera nostras, 1914 (with BUSSON).

6) Wiener klinische Wochenschrift 1917.

7) Centralbl. f. Bakt., I, Orig., vol. 74, 1914.

8) Ned. Tijdschr. v. Geneeskunde 1918, II, 1911.

faction are both checked by the appearance of the acid in the nutrient medium.

3. The virtual gelatine-liquefaction-halo, which one can construct by means of EIJKMAN's gelatine-stripe method [1]), is, it is true, not congruent with the haemodigestion-halo in the blood-agar plate; but on the oxyhaemoglobin plate the halos come very nearly together.

4. The strains that are strongly haemodigestive consume casein also intensely; the identity of the casein-digestive and the gelatine-liquefying ferment has been made very plausible by EIJKMAN, by means of the gelatine-stripe method.

SNAPPER's discovery that the digestion of blood has a much quicker process in blood-bile-agar than in blood-agar, incited me to put my hypothesis, stated before, to the test and to enlarge my investigations on the decomposition of oxyhaemoglobin by other bacteria as well.

I want to refer to the fact that the origin of the greenish and clear halo round the colonies of a haemodigestive choleravibrio on the blood-agar plate is actually based on transformation of the oxyhaemoglobin (SNAPPER entered into the details of this to confirm my previous spectroscopic research): first haematine-like bodies originate, which are decomposed in the course of the experiment.

This is also obvious in the decrease of the greenish colour near the stripe-culture, while the pyridin-chromogen reaction takes place slower at that point than at a greater distance from the culture.

On oxyhaemoglobin plates on which, as I pointed out before, the process of the digestion of the oxyhaemoglobin is to be seen clearly with the naked eye by the zones of different colour, it is possible too to indicate the further decomposition of haematin by means of pyridin and sulphurammonium. On the blood-bile-agar plate the cholera vibrio is sustained in the digestion of the oxyhaemoglobin.

By the action of the bile on the blood, the haemoglobin has not only come out (as is the case in the oxyhaemoglobin plate), but has been transformed into haematin-like substances besides. The process of decomposition is progressing already considerably when the cholera vibrio begins to influence it, which is revealed in the quick formation of a broad clearly transparent and colourless halo round the

---

[1]) The gelatine stripe method is executed by bringing, by means of a platinum-loop, stripes of liquefied gelatine close to the culture on the agar plate. The gelatine becomes solid at an ordinary temperature; so it is possible to trace how far the gelatine stripe (after some time at 22° C. e.g.) disappears from the culture by the action of a ferment.

The figures in this text show how one may construct the gelatine liquefying halo in this way. (In Fig. 1 e.g. the white dotted line).

stripe-culture as an expression of its haemodigestive power. Even choleravibrios that influence the blood-agar-plate exceedingly slowly, are able to form a halo on the blood-bile plate. I tried this halo-formation of the choleravibrio on the blood-bile-agar plate by means of the gelatine-stripe method and compared this one with the halos on blood plates and casein plates.

The result of these experiments which I made with several new and old cholera strains of a very divergent haemodigestive character, is shown half schematically in the following figures.

Fig. 1.

Fig. 2.

Fig. 1. The virtual (white dotted) gelatine-liquefying halo lies considerably beyond the halo of the haemodigestion on the blood-agar plate.

Fig. 2. The zones approach each other very clearly on the oxy-haemoglobin plate; in some cases (as is shown on the figure) there is already an indication of transformation of the oxyhaemoglobin, whose line of demarcation is congruent with the halo of the gelatine-liquefaction.

Fig. 3. *The halos of further oxyhaemoglobin transformation and gelatine-liquefaction are quite congruent on the blood-bile-agar plate,* a condition which agrees with that on the casein plate. (Fig. 4).

By this fact the identity of the oxyhaemoglobin-digestive, casein-digestive and gelatine-liquefying ferment of the cholera vibrio is confirmed.

There is this profitable difference between the blood-bile-agar plate and the blood-agar plate, that the process of haemolysis does not take place in the former.

In this way I was able to compare haemodigestion and gelatine-liquefaction within the group of Proteus-bacteria.

All the Proteusstrains which I have at my disposal (e.g. some indol-producing representatives of *Bacterium vulgare Hauseri, Pro-*

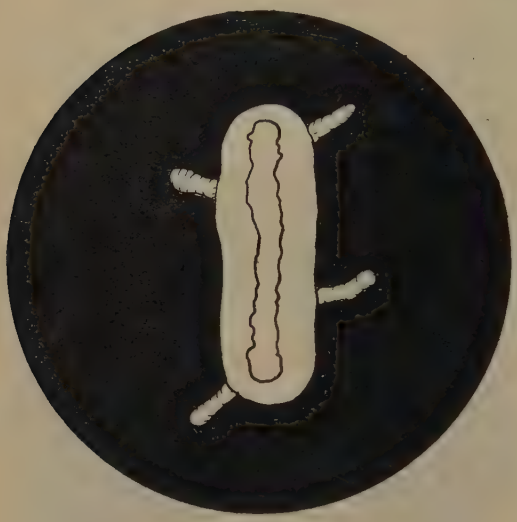


Fig. 3.

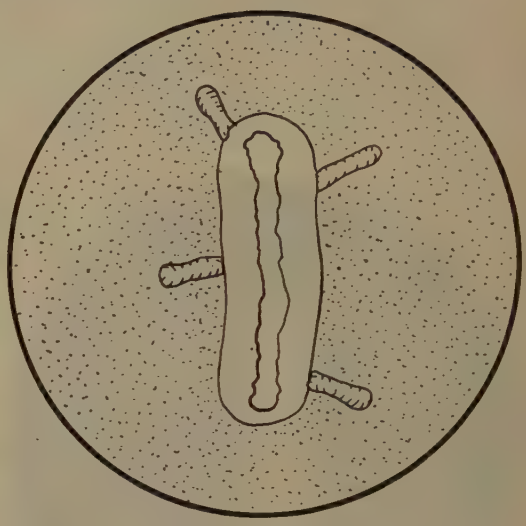


Fig. 4.

teus X_{19} of WEIL and FELIX producing indol as well and several representatives of the *Bacterium anindologenes* distinguished by me as a separate species) are *haemolytic*, that is to say, they form a halo of blood-agar and cause the oxyhaemoglobin to come out from the blood-broth.

They do not all liquefy gelatine. The an-indologenic strain Pneumaturia, which liquefied gelatine strongly 16 years ago, lost this power long ago. *This strain is the only one forming no halo on the blood-bile agar plate.* Other facts may be added to this argument for the conception that also within the Proteus group, oxyhaemoglobin-digestion and gelatine-liquefacting are caused by the same ferment: only the non-haemodigestive Proteus-strain does not digest the casein, as the others do and the liquefaction halos, constructed by means of the gelatine-stripe method are congruent with the halos of haemodigestion on the blood-bile plate.

Moreover I mention the experiments on *B. prodigiosus*, a gelatine-liquefying *coccus* from the air, *B. anthracis*, *Vibrio dunbar*, all of them haemodigestive and liquefying the gelatine, opposed to *B. typhi*, *coli*, *B. paratyphi A.* and *B.*, *B. pseudo-tuberculosis rodentium*, *B. dysenteriae* SHIGA and FLEXNER, which do not form a halo on the

blood-bile plate and do not cause the gelatine to liquefy. Both these results are in favour of the identity of the actions in question.

I want to make one more remark; as I pointed out before, sometimes one sees in an organism, of which the casein halo and the gelatine halo cover each other entirely on a nutrient medium, that their congruence has disappeared on another nutrient medium.

When glycerine has been added to the casein plate, on which the cholera vibrio is inoculated, the virtual halo of liquefaction will remain at some distance within the halo of casein-digestion.

So I observed also that the halo of gelatine-liquefaction in a strongly haemodigestive coccus, isolated from the air, is a little larger than the halo of the haemodigestion (on the blood-bile plate). The above-mentioned experimental experience teaches us that this does not contain an argument against the identity of the haemodigestive and collolytic bacterial action.

I conclude by remarking that these experiments teach us that the blood-bile plate as well as the casein plate may serve for the substitution of the broth-gelatine in determining bacteria. This is an advantage while working in tropical littorals, where the use of the nutrient media is subject to difficulties owing to the high temperature of the air.

Amsterdam,
March 1920.

Institute of tropical hygiene, department of the Colonial Institute.

Physics. — *"Remark on the possible existence of binding rings in diamond."* Communication N°. 4 from the Laboratory of Physics and Physical Chemistry of the Veterinary College at Utrecht. By Dr. N. H. KOLKMEIJER. (Communicated on behalf of Prof. W. H. KEESOM, Director of the Laboratory, by Prof. H. KAMERLINGH ONNES).

(Communicated at the meeting of January 31, 1920).

§ 1. Some years ago DEBIJE and SCHERRER [1]) investigated, whether the assumption of the existence of "binding rings" of 2 electrons each between the carbon-"ions" in diamond, was in accordance with the intensities of the beams of X-rays, reflected by some planes of the lattice as calculated on BRAGG's pattern.

For some time I have doubted however, whether the conclusion of DEBIJE and SCHERRER, that the mentioned binding rings in diamond do not exist, might be regarded as right. In their calculation DEBIJE and SCHERRER use an approximating representation, treating the two electrons of each binding ring as coinciding in their mutual centre of mass. Now I found, that the introduction of this simplification may be of great influence on the results obtained.

These considerations induced me to calculate the relative intensities of the lines in the Röntgenogram obtained by the method of DEBIJE and SCHERRER and that without neglecting the real positions of the electrons in the binding rings. The comparison of these calculations with the observed intensities might give the solution of the question, whether these intensities are in agreement with the assumption of the binding rings. Eventually it might also enable us to deduce the radius of the binding rings. Proceeding in this way I found that without making new assumptions the conclusion of DEBIJE and SCHERRER must be accepted. At the same time however I got the impression, that the observations at our disposition on diamond only do not permit the drawing of a definite conclusion. This is evident, as the reflection of the X-rays is effected not only by the eventual binding electrons, but also by the electrons circulating about the nucleus (and perhaps even more or less by the eventual electrons

[1]) P. DEBIJE and P. SCHERRER, Physik. ZS. 19 (1918) p. 476.

within the nucleus). Moreover the structure-pattern of the crystal is not the only factor that influences the intensities of the RÖNTGEN-beams reflected by the different planes, but there are more factors viz. the polarisation –, the number of planes –, the temperature- and the summation-factor calculated for this case by DEBIJE and SCHERRER.

I therefore thought it better to wait with my conclusion till I had finished the measurements on other elements with diamond-structure. As such Si, Ti and grey Sn [1]) in the first place came into consideration [2]). By these measurements I hoped to be able to separate better the different influencing factors.

As however in these Proceedings XXII p. 536 COSTER has treated the question of the binding rings, my considerations and calculations may be already of some interest, especially as in some principal points and in the conclusion they do not agree with COSTER's paper. When my measurements on this subject are finished I hope to come back to the question.

§ 2. In the main DEBIJE and SCHERRER base their declining conclusion on the fact, that the line (222) that fails on the photos, should be one of the most intensive according to the simplified model. This is directly evident from fig. 1 taking the distribution of the particles over the planes into consideration. Here the full lines indicate the relative positions of the planes (111) or (222) of the nuclei with the inner BOHR-circles concentrated in them. The broken lines represent the binding rings concentrated in their centre.

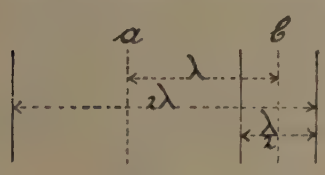


Fig. 1.

When however the approximation is used no longer, each plane a remains unchanged, each plane b is split up into 6 planes that oscillate.

When we want to investigate how this influences the structure-factor, we must know the simultaneous positions of the pairs of electrons of the different rings.

When we wish thereby to take into consideration the symmetry of the point-system, where now moving elements occur, the symmetry-elements which could be called "axis of rotation", "screw-axis"

---

[1]) A. J. BIJL and N. H. KOLKMEIJER. These Communications N°. 2*b*. These Proceedings 27 (1918) p. 359.

[2]) Rightly COSTER remarks (These Proc. XXII p. 541) that also measurements on *Ge* would be of interest.

and "plane of symmetry" are no more sufficient. Besides the position of the particles it is necessary to take also into consideration the time. For moving point-systems we may then introduce as analogous to the screw-axis a *time-axis of rotation* with n periods, with the meaning that the system becomes equal to and similarly placed with itself after a momentaneous rotation of $\frac{360^\circ}{n}$ in a definite sense round that axis, followed by a certain time-interval. It is apparent that the above mentioned moving system can have such axes, namely ternary ones. According to the sense of rotation of $\frac{360^\circ}{n}$ the time interval in question is then $\frac{2}{3}$ or $-\frac{2}{3}$ period of the electrons. For the configuration of the electrons in the binding rings then only the following possibility remains:

1st. Looking from a nucleus the sense of circulation in the four surrounding rings is the same;

2nd. Consider a plane through two of the lines connecting one nucleus with the four surrounding nuclei. When an electron of the ring round one of these lines passes this plane, this is also passed by an electron of the ring round the other line and that in the opposite direction. In this case the electrons in parallel rings have the same phase, in non parallel ones the phases are connected by a simple relation.

Now introducing into the discussion of the time-space-symmetry as analogue of a plane- and centre- of symmetry, a *reversal-plane* resp. *centre of symmetry* viz. a plane (centre), which acts momentaneously as a mirror for the point system, while also at a definite moment all velocities are reversed [1]), the above discussed system has also three quaternary reversal mirror-axes of rotation and six reversal-planes of symmetry.

§ 3. Now we can easily prove that the radius of the binding rings may be chosen in such a way that the structure-factor for the plane (222) will be nearly 0 at every moment and not a maximum, as was obtained by D. and Sch. with their approximation.

---

[1]) This proceeding is analogous to the operation of reflection by a plane or a centre, where resp. one or three coordinates change their sign, while the time must be kept constant. This is evident when the reversal of all velocities is regarded as the "changing of the sign of the time at a certain moment" or as the "reflection of the time in a definite moment". In connection with this is also the assumption of a definite sense of rotation for a time-axis of rotation.

In fig. 2 a and the full lines have the same meaning as in fig. 1. The nucleus Q is surrounded by 4 nuclei, one of which is P. R is another one and S and T have not been drawn. Let QS and QT rotate about PQ until they coincide with QR. Then the binding rings about QR, QS and QT coincide too. The above mentioned relation between the phases is now so, that in those coinciding rings the pairs of electrons form a regular hexagon. The positions of the planes b' and b'' into which the planes b of fig. 1 are split up are not changed by this rotation. In fig. 2 the phase has been chosen in such a way that those 6 planes form pairs that coincide and so give the three planes b' and b'', the construction of which needs no further explanation. In reality the hexagon $p\,q\,r\,s\,t\,u$ is perpendicularto QR and at equal distances from Q and R. In the fig. it has been represented as shifted downwards and clapped down on the plane of drawing by a rotation about a diameter perpendicular to QR. The hexagon $A\,B\,C\,D\,E\,F$ is the projection of the former on a plane perpendicular to the plane of drawing through PQ and clapped down on this plane by a rotation about this line.

When now the radius of the rings has been chosen so, that b'' falls halfway between b' and a, the structure factor of (222) in the phase represented in the figure will become zero. From the construction it is evident that the radius must be chosen $\frac{1}{\sqrt{6}}$ or $\frac{1}{2{,}45}$ times the distance between two nuclei. It is found that in that

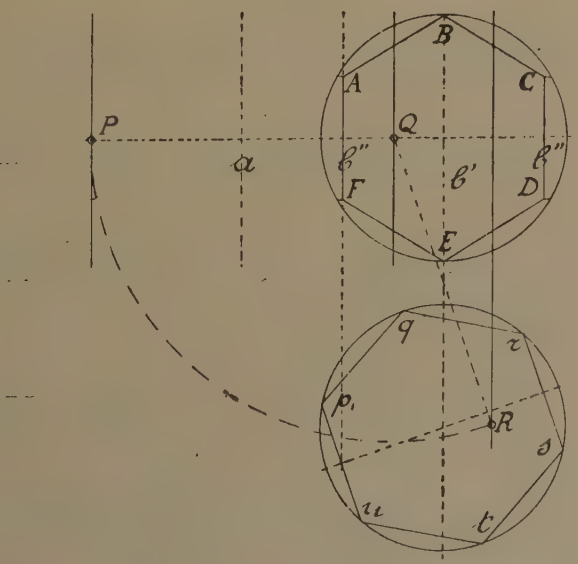


Fig. 2.

case the value of that factor remains small also for other phases, especially when the radius has been chosen a little greater. This would meet the chief objection of D. and SCH. to the binding rings as has also been shown by COSTER with a somewhat different way of representation.

§ 4. For the calculation of the intensities of the other reflected beams I proceeded in the following way:

As a consequence of the smallness of the remaining inner ring of two electrons (of one *quantum* probably for each electron) compared with the binding rings (that are perhaps of two quanta for each electron) I assumed in the calculation of the intensities of the other lines the radius of the first ring to be zero and that ring to give then a "diminishing-factor", analogous to that of D. and SCH. [1]), while also for nucleus + ring a temperature-factor had to be assumed. All this was comprised into the "diffraction-factor" $A\,(<2)$ for nucleus + ring. In the same way the factor $B\,(<1)$ referring to each of the binding electrons comprised also the temperature factor of these electrons.

Replacing $\frac{8\pi r}{\sqrt{6}}$ by v we find then at the moment t for $^1/_8$ of the structure-factor for unmixed triplets

$$\begin{aligned}
\tfrac{1}{8}S = {} & \frac{A}{2} + \frac{A}{2}\,e^{\frac{\pi i}{2}(h_1+h_2+h_3)} + \\
& + Be^{\frac{\pi i}{4}(h_1+h_2+h_3)}\Big\{\cos\tfrac{1}{2}v\left[h_1\cos\omega t + h_2\cos\left(\omega t+\frac{2\pi}{3}\right)+h_3\cos\left(\omega t+\frac{4\pi}{3}\right)\right]+ \\
& + e^{\frac{\pi i}{2}(h_2+h_3)}\cos\tfrac{1}{2}v\left[h_1\cos\omega t - h_2\cos\left(\omega t+\frac{2\pi}{3}\right)-h_3\cos\left(\omega t+\frac{4\pi}{3}\right)\right]+ \\
& + e^{\frac{\pi i}{2}(h_3+h_1)}\cos\tfrac{1}{2}v\left[-h_1\cos\omega t + h_2\cos\left(\omega t+\frac{2\pi}{3}\right)-h_3\cos\left(\omega t+\frac{4\pi}{3}\right)\right]+ \\
& + e^{\frac{\pi i}{2}(h_1+h_2)}\cos\tfrac{1}{2}v\left[-h_1\cos\omega t - h_2\cos\left(\omega t+\frac{2\pi}{3}\right)+h_3\cos\left(\omega t+\frac{4\pi}{3}\right)\right]\Big\}.
\end{aligned}$$

In this expression we may substitute the unmixed indices-triplets of the lines that were to be seen on a photo of D. and SCH., take the modulus-square, multiply this by dt, integrate this over a period

[1]) P. DEBIJE and P. SCHERRER, l.c.

and finally divide it by $\frac{2\pi}{\omega}$. In this way a measure for the intensity of the lines is obtained. The squares and products of cosines obtained in this calculation were transformed into a sum of cosines. Thus we find the following expressions, while further $\frac{\overline{|S_{002}|^2}}{64}$ and $\frac{\overline{|S_{024}|^2}}{64}$ duly got the value 0.

$$\frac{\overline{|S_{111}|^2}}{64} = \tfrac{1}{2}A^2 - AB\sqrt{2} + \tfrac{5}{2}B^2 + \frac{3B^2}{2}J_0(2v) + 3B^2J_0(v\sqrt{3}) + (3AB\sqrt{2} - 3B^2)J_0(v)$$

$$\frac{\overline{|S_{022}|^2}}{64} = A^2 + 4B^2 + 2B^2J_0(v\sqrt{12}) - 6B^2J_0(2v) + 4ABJ_0(v\sqrt{3}) - 4ABJ_0(v)$$

$$\frac{\overline{|S_{113}|^2}}{64} = \tfrac{1}{2}A^2 + 2B_2 + \frac{B^2}{2}J_0(4v) + 2B^2J_0(v\sqrt{13}) + B^2J_0(v\sqrt{12}) + 2B^2J_0(v\sqrt{7}) +$$
$$+ (AB\sqrt{2} + \tfrac{1}{2}B^2)J_0(2v) + (B^2 - 2AB\sqrt{2})J_0(v\sqrt{3}) - (AB\sqrt{2} + B^2)J_0(v)$$

$$\frac{\overline{|S_{004}|^2}}{64} = A^2 + 8B^2 + 8B^2J_0(4v) - 8ABJ_0(2v)$$

$$\frac{\overline{|S_{133}|^2}}{64} = \tfrac{1}{2}A^2 + 2B^2 + B^2J_0(v\sqrt{28}) + B^2J_0(v\sqrt{27}) + \frac{B^2}{2}J_0(4v) - 2B^2J_0(v\sqrt{13}) -$$
$$- B^2J_0(3v) + (2AB\sqrt{2} + 2B^2)J_0(v\sqrt{7}) + \left(\frac{B^2}{2} - AB\sqrt{2}\right)J_0(2v) + AB\sqrt{2}J_0(v)$$

$$\frac{\overline{|S_{222}|^2}}{64} = \tfrac{5}{2}B^2 + \tfrac{3}{2}B^2J_0(4v) + 3B^2J_0(v\sqrt{12}) + 9B^2J_0(2v)$$

where $J_0(x)$ represents a BESSEL-function of order 0.

By trials I found that $\frac{\overline{|S_{222}|^2}}{64}$ is small, when v is in the neighbourhood of 1,63 or when r is about $\frac{1}{2{,}72}$ times the distance of the nuclei (comp. the result obtained from fig. 2). This value is of the order of magnitude that would correspond to a ring with two quanta for each electron, namely $\frac{1}{1{,}94}$ times the distance of the nuclei. Supposing that the ring has exactly two quanta we obtain the following expressions:

$$\frac{\overline{|S_{111}|^2}}{64} = \tfrac{1}{2}A^2 - 1{,}16\,AB + 0{,}67\,B^2$$

$$\frac{\overline{|S_{022}|^2}}{64} = A^2 - 1{,}84\,AB + 6{,}18\,B^2$$

$$\frac{\overline{|S_{113}|^2}}{64} = \tfrac{1}{2} A^2 + 0{,}62\, AB + 1{,}62\, B^2$$

$$\frac{\overline{|S_{044}|^2}}{64} = A^2 + 2{,}41\, AB + 6{,}99\, B^2$$

$$\frac{\overline{|S_{133}|^2}}{64} = \tfrac{1}{2} A^2 + 0{,}98\, AB + 1{,}69\, B^2$$

$$\frac{\overline{|S_{222}|^2}}{64} = 0{,}16\, B^2$$

The rather small intensity found in this way for the line referring to the plane (222) seemed not irreconcilable with the observations.

§ 5. Before the calculation and the observation can be compared we must multiply the expressions found in § 4 by the polarisation-factor, the plane number-factor, and the modified summation-factor. Just as well we can equalize the above expressions with the intensities obtained by DEBIJE and SCHERRER corrected for the absorption in the rod and after division by the product of the three factors. In this way we obtain the following equations where k is a proportionality factor

$$A^2 - 2{,}32\, AB + 1{,}34\, B^2 = 2391\, k \quad \text{for (111)}$$
$$A^2 - 1{,}84\, AB + 6{,}18\, B^2 = 913\, k \quad \text{,, (022)}$$
$$A^2 + 1{,}24\, AB + 3{,}24\, B^2 = 610\, k \quad \text{,, (113)}$$
$$A^2 + 2{,}41\, AB + 6{,}99\, B^2 = 483\, k \quad \text{,, (004)}$$
$$A^2 + 1{,}96\, AB + 3{,}38\, B^2 = 446\, k \quad [1] \text{,, (133)}$$

A must decrease here: firstly exponentially with $H^2 = h_1^2 + h_2^2 + h_3^2$ by the heat motion. As coefficient of H^2 in the exponent of e we chose one of the values given by DEBIJE and SCHERRER l.c., viz. the largest one, that which is derived on the assumption of the existence of a zero energy and which appeared to have the greatest advantage for the assumption of binding rings. Secondly A must decrease with H^2 because of the two remaining electrons acting as "sphere of electrons".

For the sake of simplicity I supposed that the action of these

[1]) In the table on p. 481 of the cited paper of D. and Sch. there evidently occur some typographical errors. In column 6 2,04 must be about 4.02, 11.56 about 6 and in column 7 13 must be about 22.

two electrons might be regarded as that of a sphere over the whole surface of which the electrons circulate uniformly. The formula for the diminishing-factor then becomes $\frac{\sin \frac{2\pi\varrho}{a} H}{\frac{2\pi\varrho}{a} H}$, where ϱ is the radius of the spherical surface in question and a the edge of the elementary cube, so that we must put for A:

$$A = 2\, e^{-4{,}5 \,.\, 10^{-8} H^2} \frac{\sin \frac{2\pi\varrho}{a} H}{\frac{2\pi\varrho}{a} H}.$$

For the electrons of the binding rings we have only to attend to the heat motion. Thus I replaced B by $e^{-\alpha^2 H^2}$.

When we compare the righthand sides of the equations, that of the first, viz. that for (111), is exceedingly large. When however we compare the left hand sides, the terms containing B show that in the equation for (111) this left hand side will become smaller than the left hand sides of the other equations. This difficulty will however not be met with, when α^2 is chosen so great, that the terms with B may be neglected. This comes about to the same as the ascribing of the decreasing of the line intensity with H^2, observed by DEBIJE and SCHERRER, only to the circulation of the two remaining electrons about the nucleus. I calculated that for the radius of the spherical surface over which as a mean these electrons may be regarded to move, the value $0.075a$ had then to be chosen. This is about thrice the radius of the BOHR-ring (one-quantum for each electron) about the nucleus. This would not be an improbable value of the radius of that sphere. Then however we must take α^2 at least equal to 0,6 in order to find somewhat fitting solutions of the equations. When we put $\alpha^2 = \frac{2\pi^2 r^2}{a^2}$ (r = mean deviation by the heat motion) r should thus become somewhat smaller than $0{,}2\,a$ and such a great deviation seems to be in contradiction with recent conceptions on the specific heat of solid bodies, to which the electrons contribute to a small degree only. We may lower the α-value wanted by taking for the radius of the electronic sphere about the nucleus 4 or 5 times instead of 3 times the radius of a ring of one quantum; then however this radius becomes improbably large and α^2 remains still too large.[1])

[1]) In my opinion COSTER l.c. would also have met with these difficulties when

Summarizing, I am inclined to reject with DEBIJE and SCHERRER the existence of the binding rings in diamond as long at least as no other assumptions give us another insight into this question. Meanwhile investigations (comp. § 1) on other tetra-valent elements, perhaps also on solid hydrogen are desirable in order to obtain more detailed indications on the configuration of the electrons in the electronic sphere.

---

only he had continued his calculation so far that a direct comparison with the experimental data had been possible.

Chemistry. — *"The aluminates of sodium. Equilibriums in the system $Na_2O—Al_2O_3—H_2O$"*. By Dr. F. GOUDRIAAN. (Communicated by Prof. J. BÖESEKEN).

(Communicated at the meeting of April 23, 1920).

Introduction.

In a preceding paper[1]) a survey was given of the equilibriums that may arise at 30° in the system: $Na_2O—ZnO—H_2O$. Among other things the range of existence of the zincate of sodium and the stability-relation between ZnO and zinchydroxide were determined in this paper. In view of our still very slight and incomplete knowledge concerning the corresponding compounds of other metals, it was now tried also to determine similar equilibriums of some of these metals. The following will give a brief survey of the results obtained in the system: $Na_2O—Al_2O_3—H_2O$.

Although the existence of aluminates has long been suspected and in nature some even seem to occur in a crystallized state in some minerals (e. g. the spinels), not a single exact datum regarding these bodies is to be found in the literature. To be sure it is known that also in elaborating the mineral bauxite by treating it with soda, aluminium is fixed as an aluminate, but we are by no means acquainted either with the composition or with the stability of these compounds. It is true that several investigations have been made in this direction, but in none of these the solid phases have been isolated. The compositions that are therefore given to the aluminates have been determined in a more or less indirect way and serious objections may always be raised to the methods applied in doing so. Therefore it is not wonderful that the results are often in serious mutual contradiction. A short summary of the knowledge obtained up till now about the aluminates, from which this will further appear, is the following:

CAVAZZI[2]) first suspected the existence of these compounds and ascribed to them formulae like: $NaAlO_2$, on the ground of his observation that 1 gram-atom Al will dissolve in 1 gram-molecule NaOH.

---

[1]) Proceedings XXII, 179 (1919).

[2]) Gazz. chim. ital. **15**, 205 (1885).

Similar observations were made by PRESCOTT [1]) and LYTE [2]). A long time afterwards an investigation was made into the value of the molecular-weight of the sodium compound by NOYES and WITHNEY [3]), on the basis of the lowering of freezing point which would occur in dissolving Al in NaOH. As however no perceptible lowering in the freezing-point took place and therefore the number of particles before and after the dissolution had to be equal, they determined upon the composition: $NaAlO_2$; this compound was supposed to be divided into two ions and so to form just as many particles as the original NaOH molecules. It need not be demonstrated any further that this reasoning is uncommonly weak and little suitable as a powerful argument in favour of the composition $NaAlO_2$.

HERZ [4]) ascribes the composition: Na_3AlO_3 and K_3AlO_3 to the aluminates, because in solution he found the proportion $Na : \frac{Al}{3}$ equal to 1 : 1. On the ground of similar experiments WOOD [5]) on the other hand again arrives at the composition: $NaAlO_2$; although from his figures the proportion $NaOH : Al_2O_3$ often proves much larger than would agree with this composition.

HANTZSCH [6]) performed some conductivity measurements in aluminate solutions of various concentrations and concludes from these that the aluminates behave like salts of mono-basic acids. With such salts, which are even hydrolized to a great extent in fairly concentrated solutions forming partly colloidal $Al(OH)_3$, the conductivity-method entirely loses its value. We are not even sure of the nature of the ions present. HANTZSCH's observations therefore cannot teach us anything of the composition of these salts.

Finally we may still mention that SLADE [7]) tried to find out the composition by applying the law of mass action to aluminate solutions that are in equilibrium with $Al(OH)_3$. His reasoning does not hold exactly, because in diluted solutions the solubility of $Al(OH)_3$ is extremely slight, so that small observation errors become of very great influence on the final result. In the strong NaOH solutions of comparatively large viscosity, in which the solubility can be measured very well, it becomes inadmissible to apply the law of

---

[1]) Journ. Amer. Chem. Soc. **2**, 27.
[2]) Chem. News **51**, 109 (1885).
[3]) Zeitschr. f. phys. Chem. **15**, 694 (1894).
[4]) Zeitschr. f. anorg. Chem. **25**, 155 (1900).
[5]) Journ. Chem. Soc. **93**, 411 (1908).
[6]) Zeitschr. f. anorg. Chem. **30**, 296 (1902).
[7]) Zeitschr. f. Elektroch. **17**, 261 (1910).

mass action. A proper equilibrium-constant is therefore not to be expected.

The only exact datum concerning the composition of the aluminates is the melting-diagram of the system: $CaO—Al_2O_3$ determined by SHEPHERD and RANKIN [1]). From this diagram there proved to be four compounds between these components.

The modifications in which aluminiumhydroxide may occur.

In a similar way as described in the preceding paper, I tried to determine the solubility-curves (p and T constant) in this system. Also here the determinations were executed at 30,0° C. The NaOH used had been prepared from sodium, the water had been distilled and boiled immediately before use. The aluminiumhydroxide was prepared in various ways, for it is known that *according to the preparation this compound shows different properties.* The products used had been prepared as follows:

A. Aluminiumhydroxide.

Product α was obtained by precipitating an aluminium salt (sulphate or chloride) with the required quantity of ammonia. The very voluminous, gelatinous precipitate was consequently sucked out and completely washed out, which took a long time. The gellous mass obtained in this way was dried at 130°—140°; after that it made the impression of a shrivelled up gellous mass and was very hard and glassy. Such a product does not possess a constant composition, the water-percentage varies according to the duration of heating. In the case of the product used, the time of heating had been chosen in such a way that the composition agreed as much as possible with $Al(OH)_3$. The water-percentage amounted to: 33,81 % (theoretically for $Al(OH)_3$ to .... 34,57 %). The particles of this product display no or hardly any perceptible swelling even after having been shaken a long time with distilled water. If however they are in contact with NaOH-solutions stronger than ± 2 normal, they again swell very rapidly into a very voluminous product. This phenomenon renders the reaching of equilibrium particularly difficult: the swollen particles settle down very slowly.

Product β. In quite a different state aluminiumhydroxide can be obtained by issuing from the solution of an aluminate. If we gradually decrease the alkalinity by carefully adding a diluted, weak acid (introducing CO_2 e. g.), then the hydroxide precipitates in a very compact, crystalline-looking form. Indications for the existence of

[1]) Zeitschr. f. anorg. Chem. 68, 370 (1910).

this form are to be found with various investigators [1]); VAN BEMMELEN ascribes to this product the formula: $Al_2O_3 3H_2O$; later on it was once more examined by RUSS [2]). The latter arrives at the same formula and finds that the separation will take place the sooner and the more completely as the proportion $Na_2O : Al_2O_3$ in the solution more closely approaches the value: 1,24 : 1.

The most suitable preparation of this form of the hydroxide appeared to me the following. To a solution of 25 Grs. of NaOH in 110 cm^3 of water, 13,5 Grs. of aluminium are added in small quantities at a time. When the reaction is finished, the solution is quickly filtered and after that left open to the air for some days. Soon already the hydroxide begins to precipitate and as under the continued influence of the CO_2 from the air the OH'-ions concentration decreases, the quantity of hydroxide gradually increases. Finally the product is filtered and completely washed out; it displays absorption of ions in a much smaller degree than product α, so that the purifying is greatly facilitated. RUSS mentions that his product, even at a 500 fold magnification, did not distinctly prove crystalline; nor was this the case with the product obtained by me. At a 600 fold magnification a distinct crystalline structure was not perceptible. Therefore the opinion of former investigators, that here we have a crystalline form of the hydroxide, is premature as yet.

Analysis of the product, after drying at 110° to constant weight, yielded: 34,29 % H_2O .... 65,62 % Al_2O_3, corresponding with the composition: $Al_2O_3 . 3\,H_2O$. Carbonic acid could not be indicated, so that the at first not improbable supposition, that perhaps basic carbonates of aluminium would have arisen, was not confirmed. When strongly magnified, the product also made a perfectly homogeneous impression, even when brought into prolonged contact with water, the particles do not show any swelling and do not alter externally. To their behaviour with regard to NaOH solutions, we shall revert later on, when treating the equilibriums. We may still remark that the particles are finer, more sandy and more compact as we cause the separation of the hydroxide to take place more slowly and gradually. If, for instance, we suddenly

---

[1]) BONSDORFF. Pogg. Ann. **27**, 275 (1834).
BECQUEREL. Compt. rend. **67**, 1061 (1868); **79**, 82 (1874).
KRAEMER. Archif. pharm. [2], **79**, 268 (1854).
VAN BEMMELEN. Rec. trav. chim. Pays-bas. **7**, 75 (1888).

[2]) Zeitschr. f. anorg. Chem. **41**, 216 (1904).

lead a current of CO_2 into the aluminate solution, the precipitate is perceptibly more floccose and the particles are coarser than if we cause it to arise by a prolonged exposure to the air.

Product γ. A very remarkable and, so far as I know, in the literature not yet described form of the hydroxide, arose as follows: The dessiccated particles of product α, which have quite the outward aspect of a shrivelled up gellous mass, do not swell in pure water, in *concentrated* NaOH-solutions they swell very rapidly. On being shaken a long time with diluted NaOH-solutions, they not only were found to give nos welling, but even to pass into *a fine crystallized product.* This transition succeeds best if the concentration of the lye is between 0,5 and 2,0 normal, while they are continually shaken vigorously. It usually took a few months before the transition had taken place completely. It can best be watched microscopically; the original aspect: gelatinous, very irregularly formed particles of various sizes, disappears in the long run and in their place we observe: bar-shaped crystals very regular in shape and size. No doubt we here have a crystallized phase: at a 600 fold magnification the crystals could be distinctly observed. Their length amounted to 8—20 μ, their width $\pm$ 3 μ, they are faintly double-refractive.

The remarkable phenomenon is especially that we have here *a direct transition from the gelatinous state into the crystalline state,* of which no examples have been stated with any certainty as yet. Where we see that, dependent on the OH'-ions concentration, the gelatinous mass of aluminiumhydroxide crystallizes or swells to amorphous particles, this pleads very strongly in favour of the gradual transition of the crystallized and the amorphous state of matter. This has been suspected on the ground of various phenomena, but the direct experimental proof is still wanting. The systematical study of the crystallization and swelling of such bodies as aluminium-hydroxide may probably improve our insight into this transition. Anyhow the swelling of aluminiumhydroxide as a function of the $H^{\cdot}$ and OH'-ions concentration is remarkable and a further study about this is in progress.

On using the product γ, close attention should always be paid that it no longer contains any gelatinous particles of product α, as these possess a greater solubility in lyes, so that in this case we should not measure the *exact* solubility of γ. A microscopical control of the form γ was therefore applied with all following determinations.

Analysis of the product yielded: 34,35 % H_2O - 65,52 % Al_2O_3, so corresponding with $Al_2O_3 . 3H_2O$ (after drying at 100—110°).

B. Aluminiumoxide.

The three products of Al_2O_3 that received consideration had respectively been obtained by careful, not too long heating at 300°—400° of the products α, β and γ. Long heating was avoided, because this makes the oxide very indifferent, so that it delays the reaching of equilibrium, nay, may even render it impossible. Taken in the same order, in the following these products will be indicated as δ, ε and ξ.

Product δ, which had been obtained out of α, still made quite the impression of a shrivelled up, gelatinous mass; in NaOH-solutions the particles again proved capable of swelling or crystallizing dependent on the concentration.

The particles of product ε microscopically displayed entirely the same aspect as those of β. The crystals of γ proved to alter on heating; the oxide ξ was not distinctly crystalline.

The equilibriums of aluminiumhydroxide with NaOH-solutions of various concentrations.

The determination of these equilibriums yielded very great difficulties. The cause of this is partly the occurrence of the hydroxide in various forms, partly also the viscosity of the solutions on great NaOH concentration. Owing to this, we are in the first place compelled with each determination to carefully state what solid phase is present in the state of equilibrium, which is very often impossible by a direct way. In many cases the rest method is applied. Further we should continually control whether the values found really hold good for the state of equilibrium, in other words whether this state has perfectly arisen. This takes a long time, especially in the more concentrated solutions; many determinations could only yield reproducible figures after having been shaken in the thermostat for 2 or 3 months. The depositing of the solid phases also requiring much time, this is the reason that the whole investigation takes up a very long time.

A survey of the determinations performed is to be found in fig. 1 and table I. The curves I, II and III in fig. I refer to determinations performed with the products α, β and γ respectively. In fig. II (page 140) they are indicated by *CF*, *BE* and *AD*. In the third column are indicated the solid phases which, when the experiments are performed, were added to the NaOH-solutions; in the tenth column those which proved present after reaching the equilibrium. As will be proved, some equilibriums must be considered metastable.

Let us first consider the equilibriums of the gelatinous hydroxide (α) with NaOH-solutions of various concentrations. In the more concentrated solutions the particles swell very much and show a solu-

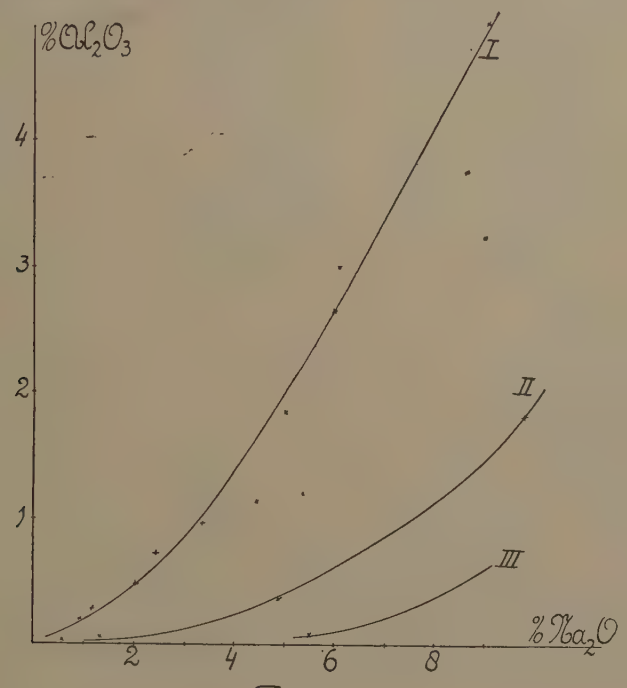


Fig. 1.

bility that is considerably greater than that of the other forms of the hydroxide. Although in diluted solutions crystallization to product γ arises very slowly, the rapidity of this transition is so slight, that after one or two months we still entirely measure the solubility of the gelatinous particles α. Most of the determinations performed with product α therefore form together the curve I; some that greatly deviate from this curve (see Nos. 10 and 11) have not been analysed till after a considerably longer time than the others. A considerable percentage of α had consequently been converted into γ. Yet these points 10 and 11 are still situated far *above curve III*, which represents the solubility of γ. This phenomenon requires our special attention, for if between the solid phases to which curves I and III refer, no continuous transition was possible, we then might expect to remain on curve I as long as the gelatinous phase was present and a subsequent sudden decline to curve III. The phenomenon observed here may have various causes:

a. There is a continuous transition between the solid phases of curves I and III; between these curves we must imagine quite a

TABLE I. System Na_2O—Al_2O_3—H_2O. Temperature 30,°0 C.

N°.	Former N°.	Solid phase added.	Composition of the solution			Composition of the rest			Nature of the solid phase in the state of equilibrium	Particulars.
			% Na_2O	% Al_2O_3	% H_2O	% Na_2O	% Al_2O_3	% H_2O		
1	29	prod. α	1.0	0.2	98.8	0.6	14.1	85.3	gelatinous particles	Partly swollen up particles of prod. α. Microscopically some bars of γ were perceptible.
2	28	ditto	2.1	0.5	97.4	1.6	16.0	82.4	ditto	
3	27	„	6.1	3.1	90.8	6.9	28.8	64.3	„	
4	26	„	9.0	5.0	86.0	7.3	24.5	68.2	„	Quite gelatinous, very much swollen up.
5	1	„	6.0	2.7	91.3	4.5	30.9	64.6	„	As with 1, 2 and 3; very few bars visible.
6	2	„	3.4	1.0	95.6	2.6	24.2	73.2	„	
7	5	„	2.5	0.7	96.8	2.1	26.3	71.6	„	Very much swollen up and voluminous.
8	3	„	15.7	8.5	75.8	12.7	29.2	58.1	„	
9	6	„	8.6	3.8	87.6	7.1	28.8	64.1	„	
10	12	„	4.5	1.1	94.4	4.3	26.0	69.7	„	Determinations not performed till after 3 or 4 months after the beginning. Bars visible, still many amorphous, gelatinous particles.
11	14	„	5.4	1.2	93.4	4.6	30.7	64.7	„	
12	11	prod. β	20.4	11.2	68.4	15.8	32.3	51.9	„	Particles of prod. β. disappeared, the mass is amorphous, more or less swollen.
13	13	ditto	5.5	0.4	94.1	5.8	18.7	75.5	„	
14	15	„	18.7	9.8	71.5	15.3	41.5	43.2	„	
15	22	„	9.8	1.8	88.4	9.3	28.8	61.9	„	
16	23	„	4.9	0.4	94.7	3.6	18.3	78.1	prod. β	Particles of prod. β continue to exist quite or nearly quite unaltered. No swelling perceptible.
17	24	„	2.7	0.2	97.1	2.4	18.0	79.6	„	
18	25	„	1.4	0.06	98.54	0.5	18.2	81.3	„	
19	35	„	15.7	5.3	79.0	11.9	38.4	49.7	gelatinous particles	As with 12, 13, 14 and 15. Particles swollen up.
20	37	„	19.9	10.0	70.1	13.7	34.7	51.6	„	

TABLE II. System Na_2O—Al_2O_3—H_2O. Temperature 30,°0 C. (*Continued*).

N°.	Former N°.	Solid phase added.	Composition of the solution			Composition of the rest.			Nature of the solid phase in the state of equilibrium	Particulars.
			% Na_2O	% Al_2O_3	% H_2O	% Na_2O	% Al_2O_3	% H_2O		
21	38	prod. γ	5.5	0.08	94.42	3.3	23.8	72.9	prod. γ	Bar-shaped crystals clearly visible in all.
22	41	ditto	7.5	0.3	92.2	3.7	36.1	60.2	ditto	
23	42	„	9.4	0.5	90.1	6.7	22.0	71.3	„	
24	43	„	21.7	3.2	75.1	13.4	25.8	60.8	„	
25	30	prod. δ	9.1	3.3	87.6	8.9	14.8	76.3	gelatinous particles	Particles very much swollen up and voluminous. Microscopically some bar-shaped crystals (prod. γ) are perceptible; their quantity is greatest in the most diluted solution (27).
26	31	ditto	5.0	1.9	93.1	3.8	36.1	60.1	ditto	
27	32	„	0.5	0.04	99.46	0.9	26.4	72.7	„	
28	33	„	1.1	0.3	98.6	1.0	32.4	66.6	„	
29	44	prod. ε	3.7	0.2	96.1	2.9	27.6	69.5	„	Particles of prod. ε or β no longer clearly recognisable: mass swollen.
30	46	ditto	7.4	1.3	91.3	5.5	24.7	69.8	„	
31	47	„	9.1	1.9	89.0	6.1	31.8	62.1	„	
32	48	prod. ξ	6.3	0.2	93.5	3.6	28.8	67.6	prod. γ	Bar-shaped crystals of γ, clearly visible in all.
33	49	ditto	8.1	0.3	91.6	4.1	33.1	62.8	ditto	
34	50	„	8.9	0.4	90.7	4.3	34.0	61.7	„	
35	46	prod. α	19.9	14.8	65.3	—	—	—	diamond-shaped cryst. + gel. part.	Metastable triple-points in which gelatinous aluminiumhydroxyde coexists by the side of the aluminate $4Na_2O.3Al_2O_3.16H_2O$.
36	36	prod. β	21.1	12.9	66.0	—	—	—	diam.-shap. cryst.+ swollen part. of β.	
37	45	prod. γ	24.6	4.9	70.5	—	—	—	diam.-shap. crystals + crystals of γ.	Stable triple-point.
38	19	prod α	21.5	10.3	68.2	27.2	28.0	44.8	diam.-shap. crystals + cryst. of γ.	A great many diamond-shaped crystals of $4Na_2O.3Al_2O_3.16H_2O$ present
39	34	ditto	23.4	7.9	68.7	28.0	26.9	45.1	ditto	
40	17	„	25.3	4.3	70.4	27.6	19.6	52.8	„	

TABLE III. System $Na_2O—Al_2O_3—H_2O$. Temperature 30°0 C. (*Continued*).

N°.	Former N°.	Solid phase added	Composition of the solution			Composition of the rest.			Nature of the solid phase in the state of equilibrium	Particulars.
			% Na_2O	% Al_2O_3	% H_2O	% Na_2O	% Al_2O_3	% H_2O.		
41	21	prod. α	25.5	3.1	71.4	28.3	24.0	47.7	$4\ Na_2O.3\ Al_2O_3.16\ H_2O$	Diamond-shaped aluminate crystals
42	7	ditto	26.5	2.1	71.4	28.8	23.8	47.4	ditto	
43	16	„	27.8	0.8	71.4	29.2	25.4	45.4	„	
44	4	„	30.2	2.5	67.3	30.1	21.2	48.7	„	
45	18	„	32.5	4.3	63.2	31.3	18.0	50.7	„	
46	8	„	34.3	5.2	60.5	—	—	—	$4\ Na_2O.3\ Al_2O_3.16\ H_2O$ + $4\ Na_2O.Al_2O_3.10\ H_2O$	
47	40	„	35.3	4.0	60.7	42.2	13.1	44.7	$4\ Na_2O.Al_2O_3.10\ H_2O$	Needle-shaped aluminate crystals
48	9	„	37.3	1.9	60.8	39.2	4.9	55.9	ditto	
49	10	„	39.7	0.2	60.1	43.0	9.5	47.5	„	
50	20	„	40.8	0.1	59.1	—	—	—	$4\ Na_2O.Al_2O_3.10\ H_2O$ + $Na_2O.3\ H_2O$	
51	39	NaOH	41.9	—	58.1	—	—	—	$Na_2O.3\ H_2O$	

series of other curves relating to these continuously varying phases.

b. If we imagine the conversion of α into γ to come about, because primarily the α particles dissolve and γ crystallizes from this solution, then it is possible that these two processes take place with very unequal rapidity. If the crystallization came about very rapidly in proportion to the solution of α, the values situated between curve I and curve III would be reached.

As we said before however, the crystallization takes place extremely slowly, whereas the solution of the particles of product α happens more rapidly. Therefore explanation *b* does not hold true and as most probably it will not be easy to find a more plausible explanation, I believe I may best interpret the experiment by accepting a continuous transition between the solid phases that coexist on curves I and III with the solutions. For curve III this solid phase is the crystallized aluminiumhydroxide $Al_2O_3 . 3 H_2O$ as microscopical examination as well as analysis of the rests prove. If we consider the rests of the points situated on curve I (Nos. 1—11) it then appears that the lines that unite solutions and accessory rests, do not display a mutual point of intersection inside the triangle. The gelatinous phase that coexists along curve I by the side of the solutions, must therefore be a product of varying composition, rich in water and which besides (see analysis) has absorbed a certain quantity of alkali. Of course *curve I is quite metastable with regard to curve III*, but can be determined very well owing to the slight rapidity of transition.

If we now survey the determinations performed with product β, it appears that they form curve II, which is situated between I and III (fig. II, curve *BE*); besides the particles swell strongly in the more concentrated solutions, not appreciably in the diluted solutions. In any case we must therefore consider the form β as metastable with regard to γ; even though, in spite of numerous attempts I have not succeeded in experimentally realizing the transition $\beta \rightarrow \gamma$. Fundamentally product β has nothing remarkable, it is but one of the many forms between I and III, which forms are all metastable as regards the crystallized hydroxide γ. As to aspect, β is already much more like product γ than α; this too pleads in favour of the continuous transition of the forms into each other.

The equilibriums of Al_2O_3 with NaOH-solutions of various concentrations.

The determinations performed with the products δ, ε and ξ distinctly indicate that *at 30° Al_2O_3 is metastable as regards $Al_2O_3 . 3H_2O$.* The solutions in which product ξ was added as a solid phase, give

values that fall on curve III with satisfactory accuracy; the bar-shaped crystals of γ too proved to be present in the state of equilibrium. Consequently ξ has been hydrated and converted into γ. In pure water this hydration takes place only very slowly; in the lye-solutions however much more quickly. The cause of this is probably that in the latter solutions the Al_2O_3 dissolves primarily and the hydroxide separates from this solution.

The determinations with the products δ and ε are about situated on the curves I and II; this too shows that the hydration takes place very rapidly in proportion to the stabilisation to product γ. Besides it shows that the differences between the product α, β and γ have not disappeared after the heating, in other words that also Al_2O_3 exists in various forms. All however are metastable at 30° as regards the trihydrate.

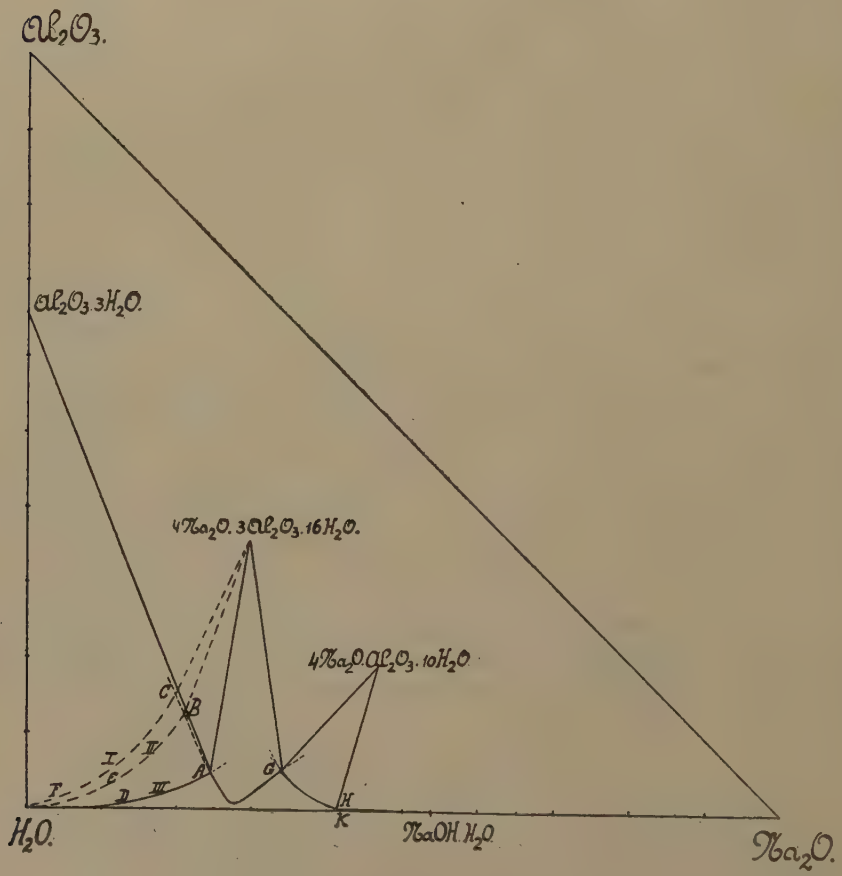


Fig. II.

The equilibriums along AG; the sodiumaluminate: 4 Na_2O . 3Al_2O_3 . 16 H_2O.

When alumiumhydroxide is dissolved in ever more concentrated solutions of NaOH, the sodiumaluminate from the above-mentioned formula crystallizes; curve *AG* in fig. II represents the solubility-curve of this salt. The compound crystallizes very well in diamond-shaped crystals; the equilibriums are reached much more easily than the others. The composition of the aluminate has in the first place been deduced from the results of the rest analyses. In the second place the wet salt was sucked out without the access of air, dried without the removal of the adhering mother-lye and analysed afterwards. The result was: 30,1 % Na_2O; 37,1 % Al_2O_3 (theoretically for the composition above-mentioned: 29,5 % Na_2O; 36,4 % Al_2O_3). As the salt forms very strongly incongruent solutions, a complete removal of the mother-lye is practically impossible. Taking this into consideration, the composition found corresponds very satisfactorily with our formula. The solubility-curve *AG* has as stable ends: on the one side *A*, the triple-point: Al_2O_3 . 3 H_2O + 4 Na_2O . 3 Al_2O_3 . 16 H_2O + solution; on the other side *G* the triple-point: 4 Na_2O . 3Al_2O_3 . 16 H_2O + 4 Na_2O . Al_2O_3 . 10 H_2O + solution. The metastable part *ABC* of the curve *AG* is partly determined; on this a series of metastable triple-points are situated, of which *B* and *C*, both indicating the coexistence of the aluminate with gelatinous hydroxide, are determined.

The equilibriums along GH; the sodiumaluminate 4 Na_2O . Al_2O_3 . 10 H_2O.

To *AG* is joined the curve *GH* relating to a second compound, an aluminate of the composition: 4 Na_2O . Al_2O_3 . 10 H_2O. Like the former compound it is well crystallized in needle-shaped crystals, which are very hygroscopical. Isolation of the pure salt yielded the same difficulties as have been described with the other aluminate. This too was sucked out with all precautions and quickly dried on porous earthenware. Analysis of the product thus obtained yielded: 47,6 % Na_2O; 18,1 % Al_2O_3 (theoretically for the above-mentioned composition 46,8 % Na_2O; 19,3 % Al_2O_3). Analysis of the rests also indicate this composition: 4 Na_2O . Al_2O_3 . 10 H_2O.

If to this solid salt we add a very slight quantity of water or diluted sodium lye, it must partly be converted into the other aluminate: 4 Na_2O . 3 Al_2O_3, 16 H_2O, while the solution gets the composition *G* (see fig. II). This conversion could very well be stated by microscope.

The stable end of the solubility-curve *GH*, the triple-point *H* indicates the coexistence: $4\,Na_2O\,.\,Al_2O_3\,.\,10\,H_2O$ + $NaOH\,.\,H_2O$ + solution.

The equilibriums along HK.

As last curve of the solubility-isotherm the curve *HK* is joined to *GH* indicating the solutions coexisting with the monohydrate of sodium-hydroxide. As the triple-point *H* is situated near: 0,1 % Al_2O_3, so very closely on the Na_2O-axis, the curve *HK* is very short. Therefore only the end points *H* and *K* have been determined.

SUMMARY.

1. At 30° two stable aluminates arise in the system Na_2O—Al_2O_3—H_2O: viz. $4\,Na_2O.\,3\,Al_2O_3.\,16\,H_2O$ and $4\,Na_2O.\,Al_2O_3.\,10\,H_2O$. Both of those form strongly incongruently saturated solutions, in other words they are decomposed by water and by diluted NaOH solutions. In fig. II we may see below what concentration-limit the NaOH-solution will cause this decomposition.

2. According to the preparation aluminiumhydroxide may be obtained in different forms. Under special circumstances it arises as a crystallized hydrate of the composition: $Al_2O_3.\,3H_2O$.

3. The gelatinous hydroxide must be considered as a metastable phase of variable composition. It absorbs variable quantities of alkali.

4. Most probably there is a continuous transition between these gelatinous hydroxides and the crystallized hydrate.

5. Aluminiumoxide is metastable at 30° as regards the hydrate.

6. The swelling that the dessiccated particles of the hydroxide and oxide display, is very much dependent on the alkalinity of the solution.

Delft,
April 1920.

Inorganic and physical-chemical Laboratory of the Technical University.

Physics. — "*Derivation of a formula for the temperature dependence of the velocity constants in gas reactions from a special image of the process.*" By Dr. J. TRESLING. (Communicated by Prof. H. A. LORENTZ).

(Communicated in the meeting of March 27, 1920).

Using a definite image of the dissociation BOLTZMANN derived a formula for the equilibrium constant in gas reactions. By means of a similar image we only need a short calculation to find the temperature dependence of the velocity constants in gas reactions.

As to the dissociation let us e.g. consider that of I_2 into $I + I$. We have then the following image of the dissociation:

A iodine atom be a centre of force. It will act on a neighbouring atom only then when their distance lies between a and $a + da$. We call a sphere with radius a the attraction sphere of the atom.

The action will be thus that at the passage of the layer da the potential energy will decrease from 0 to ψ (ψ being a negative quantity). Pairs of atoms, the mutual distance of which is less than a, will be regarded as I_2-molecules.

From the kinetic theory of gases we know the number n_1 of simple atoms and the number n_p of pairs, we may expect in the gas viz:

$$n_1 = Ae^{-hmc^2}\, du\, dv\, dw\, dx\, dy\, dz$$

$$n_p = A^2 e^{-hm(c^2+c'^2)-2h\psi}\, du\, dv\, dw\, dx\, dy\, dz\, du'\, dv'\, dw' dx'\, dy'\, dz'$$

where

$$h = \frac{1}{2kT} \qquad c^2 = u^2 + v^2 + w^2 \qquad c'^2 = u'^2 + v'^2 + w'^2.$$

A is defined by the total quantity of iodine.

Each pair the atoms of which lie in their mutual spheres of attraction forms a molecule. Let us now arbitrarily choose in each molecule one atom as the "first one" and the other as the "second one". We then see that the number of molecules n_2, the first atom of which lies in an element $dx\, dy\, dz\, du\, dv\, dw$, while the second one is situated in the element $dx'\, dy'\, dz'\, du'\, dv'\, dw'$, is given by the half of n_p [2]) viz:

[1]) E.g. JEANS. The Dynamical Theory of Gases. 2nd Ed. pg. 92 s.q.q., pg. 211 s.q.q.

[2]) Prof. LORENTZ called my attention to this factor $^1/_2$.

$$n_2 = \tfrac{1}{2} A^2 e^{-hm(c^2+c'^2)-2h\psi} \; dx\, dy\, dz\, du\, dv\, dw\, dx'\, dy'\, dz'\, du'\, dv'\, dw'$$

Introducing the coordinates of the centre of mass and the relative coordinates for a pair, viz:

$$X_z = \tfrac{1}{2}(x + x') \quad \text{etc.} \qquad X_r = x' - x \quad \text{etc.}$$
$$\xi = \tfrac{1}{2}(u + u') \quad \text{etc.} \qquad \alpha = u' - u \quad \text{etc.}$$

and putting

$$\xi^2 + \eta^2 + \zeta^2 = C^2 \qquad \alpha^2 + \beta^2 + \gamma^2 = V^2 \qquad X_r^2 + Y_r^2 + Z_r^2 = r^2$$

we find for n_2

$$n_2 = \tfrac{1}{2} A^2 e^{-2hmC^2} \; d\xi\, d\eta\, d\zeta\, dX_z\, dY_z\, dZ_z\, e^{-\frac{1}{2}hmV^2-2h\psi} \; d\alpha\, d\beta\, d\gamma\, 4\pi r^2\, dr$$

The number of atoms per unit of volume is found by integration of n_1 over u, v, w and by division by $dx\, dy\, dz$. As always further on we think namely of a diluted gas and thus find:

$$v_1 = A\left(\sqrt{\frac{\pi}{hm}}\right)^3$$

The number of molecules per unit of volume is found in the same way from n_2, namely

$$v_2 = \tfrac{1}{2} A^2 e^{-2h\psi}\left(\sqrt{\frac{\pi}{2hm}}\right)^3\left(\sqrt{\frac{2\pi}{hm}}\right)^3 \omega \quad . \quad . \quad . \quad . \quad (1)$$

where ω has been written for the volume of the sphere of attraction.

We thus find for the dissociation constant K the formula

$$K = \frac{v_2}{v_1^2} = \tfrac{1}{2}\omega e^{-2h\psi} = \tfrac{1}{2}\omega e^{-\frac{\psi}{kT}} \quad . \quad . \quad . \quad . \quad . \quad (I)$$

Passing to the velocity constants we may use the following considerations. A number of iodine molecules per unit of volume will dissociate spontaneously with a velocity proportional to the number of molecules, thus

$$\frac{dv_2}{dt} = -k_1 v_2$$

The atoms will associate spontaneously with a velocity proportional to the number of pair of atoms. By this the number of molecules will increase, thus

$$\frac{dv_2}{dt} = k_2 v_1^2$$

In the stationary state we must have therefore

$$k_1 v_2 = k_2 v_1^2 \quad \text{or} \quad \frac{v_2}{v_1^2} = \frac{k_2}{k_1} = K.$$

The value of K has been found above.

Accepting the image of the dissociation we evidently can also

easily calculate the velocity constant k_1. To find this we have to know which fraction of the molecules dissociates per unit of time or of how many of the molecules one constituent leaves the sphere of attraction of the other one per unit of time.

Consider a surface element $d\sigma$ of the sphere of attraction.

The number of atoms that passes this surface element of the sphere of attraction of the other atom per unit of time in outward direction is

$$\tfrac{1}{2}\, A^2 e^{-2hmC^2}\ d\xi\, d\eta\, d\zeta\, dX_z\, dY_z\, dZ_z \int v_n e^{-\frac{1}{2}hmV^2-2h\psi}\ d\alpha\, d\beta\, d\gamma\, d\sigma$$

where v_n represents the component of the relative velocity in the direction perpendicular to the surface.

Let us take for the α-direction the direction of the normal, then we can write for the number in question

$$\tfrac{1}{2}\, A^2 e^{-2hmC^2}\ d\xi\, d\eta\, d\zeta\, dX_z\, dY_z\, dZ_z \int \alpha\, e^{-\frac{1}{2}hmV^2-2h\psi}\ d\alpha\, d\beta\, d\gamma\, d\sigma. \qquad (2)$$

The integration limits for α, β and γ are defined in the following way.

The equations of motion of the two atoms are:

$$m\frac{d^2x}{dt^2} = -\varphi(r)\frac{x'-x}{r} \quad \text{etc.}$$

$$m\frac{d^2x'}{dt^2} = +\varphi(r)\frac{x'-x}{r} \quad \text{etc.}$$

When $\psi(r)$ represents the potential energy of the two atoms, when their distance is r, we have

$$\varphi(r) = -\frac{\partial\psi}{\partial r}.$$

By subtraction we find the equation of the relative motion

$$m\frac{d\alpha}{dt} = 2\varphi(r)\frac{X_r}{r}. \quad \text{etc.}$$

Multiplying these 3 equations respectively by α, β and γ and taking their sum, we find the equation ot energy

$$\tfrac{1}{2}\, m\frac{d(\alpha^2+\beta^2+\gamma^2)}{dt} = -2\frac{\partial\psi}{\partial r}\left(\frac{X_r}{r}\alpha + \frac{Y_r}{r}\beta + \frac{Z_r}{r}\gamma\right) = -2\frac{d\psi}{dt}$$

so that

$$\tfrac{1}{2}\, m(\alpha^2+\beta^2+\gamma^2) + 2\psi = C.$$

As to the action of the sphere of attraction we shall use the image of a hard layer against the inside of which the atoms can impinge. As long as the velocity is small, the impulses are elastic.

The layer will however not be able to resist a strong normal impulse. When the radial relative component α is great enough, the two internally colliding particles may leave each other's sphere of attraction. Here also the tangential velocity component will not change. The normal component on the contrary will.

The quantity $\frac{1}{2} m a^2 + 2\psi$ will therefore have the same value before and after the impulse.

We thus must take for β and γ the integration limits $-\infty$ and $+\infty$ and for α a positive value that satisfies $\frac{1}{2} m a^2 + 2\psi = 0$, and $+\infty$.

With these limits the integration with respect to α, β and γ gives in (2) a factor

$$\frac{\pi}{2}\left(\frac{2}{hm}\right)^2$$

Let us write S for the surface of the layer. The surface in (21) gives a factor S.

The integration with respect to ξ, η, ζ a factor

$$\left(\frac{\pi}{2\,hm}\right)^{3/2}$$

Thus we finally find for the number of molecules dissociating per unit of time and per unit of volume

$$\tfrac{1}{2} A^2 \frac{\pi}{2}\left(\frac{2}{hm}\right)^2\left(\frac{\pi}{2\,hm}\right)^{3/2} \times S.$$

Dividing this by the number of molecules (1) per unit of volume, we find the following value for the velocity constant

$$k_1 = \frac{S}{\omega} e^{2h\psi} \frac{1}{\sqrt{2\pi hm}} = \frac{S}{\omega} e^{\frac{\psi}{kT}} \sqrt{\frac{kT}{\pi m}} \quad . \quad . \quad . \quad . \quad (II)$$

while from (I) and (II) we find for k_2

$$k_2 = \tfrac{1}{2} S \sqrt{\frac{kT}{\pi m}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (III)$$

Of course the k_2 can be found in the same way as k_1.

Thus far we have supposed, that every impulse is followed by a combination. The meaning of $k_2 v_1^2$ is therefore the number of collisions per unit of time and volume. We find for it [1])

$$k_2 v_1^2 = \tfrac{1}{2} v_1^2 S \sqrt{\frac{kT}{m}}$$

in agreement with (III).

This gives therefore a verification of the equation $K = \frac{k_2}{k_1}$

[1]) E.g. BOLTZMANN, Vorl. über Gastheorie I, pag. 69.

For the logarithms of the constants we have thus the temperature functions:

$$lg\,K = -\frac{\psi}{kT} + lg\frac{\omega}{2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (I')$$

$$lg\,k_1 = \frac{\psi}{kT} + \tfrac{1}{2}\,lg\frac{kT}{\pi m} + lg\frac{S}{\omega} \quad . \quad . \quad . \quad . \quad . \quad (II')$$

$$lg\,k_2 = \tfrac{1}{2}\,lg\frac{kT}{\pi m} + lg\frac{S}{2} \quad . \quad . \quad . \quad . \quad . \quad . \quad (III')$$

Prof. F. E. C. Scheffer, whom I showed the above calculation, drew my attention to the fact that a formula as (*III'*) will not be valid as long as it does not contain a term of the form $\frac{\psi}{kT}$. Moreover he felt inclined to suppose that often two atoms, when they approach each other and impinge, do not always combine to a molecule, but only under certain conditions e. g. when the relative velocity of the particles surpasses a certain value.

The image needs only a few alterations to fit the opinion of Mr. Scheffer and to give us more general formulae than (*II'*) and (*III'*).

In order to make that an atom will only then enter the sphere of attraction of another atom when the relative velocity surpasses a certain amount, we have simply to assume just at the outside of the attraction layer still a thin layer in which the forces between the atoms are repulsive ones. An atom coming from the outside, approaching another atom and having passed the outward layer will have gained an energy ψ_1. It will however only be able to pass this layer when its kinetic energy was great enough. On its further way after having passed the inner layer, it will have gained a negative amount ψ_2 of energy.

Now we can repeat the above calculation.

(*I*) and (*I'*) remain valid when only we put $\psi = \psi_1 + \psi_2$.

To find the fraction of the molecules dissociating per unit of time and of volume, we have only to extend the integration in (2) with respect to α from a value of α satisfying $\frac{1}{2}\,hma^2 + 2h\psi_2 = 0$ to $\alpha = \infty$.

The result is a formula like II when we replace in this ψ by ψ_2. The third formula may be obtained either again by division or directly.

The three formulae thus found are

$$lg\,K = -\frac{\psi_1 + \psi_2}{kT} + lg\frac{\omega}{2} \quad . \quad . \quad . \quad . \quad . \quad . \quad (I'')$$

$$lg\,k_1 = \frac{\psi_2}{kT} + \tfrac{1}{2}\,lg\frac{kT}{\pi m} + lg\frac{S}{\omega} \quad . \quad . \quad . \quad . \quad . \quad (II'')$$

$$lg\,k_2 = -\frac{\psi_1}{kT} + \tfrac{1}{2}\,lg\frac{kT}{\pi m} + lg\frac{S}{2} \quad . \quad . \quad . \quad (III'')$$

(I'') satisfus the well known thermo-dynamic relation

$$\frac{d\lg K}{dt} = \frac{Q}{RT^2}.$$

HEMPTINNE and BEKAERT [1]) have observed a velocity constant for the reaction $(C_2H_5)_3N + C_2H_5B_r \rightarrow (C_2H_5)_4NB_r$.

Here they found a dependence on the temperature which can be represented by a formula as (III''), but not by one as (III').

The same holds for a reaction investigated by VON HALBAN [2]). KRÜGER [3]) proceeds in a calculation as we did in the first part of this paper; he thus finds temperature functions as in (I'), (II'), (III'). His model is therefore too limited. The purpose of this paper is to show how this may easily be avoided by inventing a somewhat wider model.

KRÜGER however thought the idea absolutely to be rejected, that for a combination a certain minimal velocity should be required [4]).

Of course I do not pretend that in any case a formula as (II'') or (III'') will hold. To be able to calculate a right formula, we must of course know the mechanism and as, even for the most simple dissociation, for that of hydrogen this is not the case, we shall have to content ourselves with an image.

When VAN DER WAALS derives his equation of state considering the molecules as perfectly elastic particles, he uses an image certainly not corresponding with reality. But still BOHR is of opinion that $\sqrt[3]{b}$, may be compared approximately with the radius of a ring. Just as well as nobody will deny the quantitative insight given us by the considerations of VAN DER WAALS, notwithstanding the special image, I think that the above formulae when they shall have been sufficiently tested by the experiment, will also give to some extent a quantitative insight into this phenomenon.

The above considerations have of course no relation to the theory of quanta. The specific heat corresponds to that with 6 degrees of liberty.

Physical Laboratory, Delft.

---

[1]) HEMPTINNE und BEKAERT, Zeitschr. f. physik. Chem. **28**, 236 (1898)

[2]) HANS VON HALBAN ib. LXXVII 6. p. 731—733.

[3]) F. KRÜGER, Göttinger Nachrichten, 1908, pag 318 seq.

[4]) See further: K. F. HERZFELD, "Zur Theorie der Reaktionsgeschwindigkeiten" Ann. der Phys. 59, p. 635.

Chemistry. — *"The influence of different substances on the decomposition of monoses by an alkali and on the inversion of cane sugar by hydrochloric acid."* By Prof. H. I. WATERMAN and J. GROOT. (Communicated by Prof. J. BÖESEKEN.)

(Communicated at the meeting of January 31, 1920).

When the strength of the acid and of the alkali, from which the salt is formed, are known as well as the nature of the ions, we can calculate the percentage of the hydrolysis. The decomposition of monoses by an alkali can be controlled polarimetrically, so that this method as well as the often used inversion of cane sugar gives us a sensitive means to determine the percentage of the hydrolysis.[1])

Applying the law of mass-action to the electrolytic dissociation-equilibria that occur in such a solution, we can calculate the hydrolysis. Using

$$K_{\text{phenol}} = \frac{[H^{\cdot}]\,[C_6H_5O']}{[C_6H_5OH]} = 1{,}3.10^{-10} \quad \text{and} \quad [H^{\cdot}]\,[OH'] = 1{,}2.10^{-14}$$

and assuming the hydrolysis to be weak and the non hydrolized sodium-phenolate to be perfectly dissociated, we find for $\frac{1}{10}$ N sodium-phenolate solution, $[OH'] =$ rather more than 3.10^{-3}.[2])

When the hydrolysis of the sodium-phenolate in a $\frac{1}{10}$ N solution were perfect, then $[OH']$ would be 10^{-1}. From this we learn, that of the sodium-phenolate only $\frac{100}{10^{-1}} \cdot 3.10^{-3} = 3\ \%$ is hydrolized. For more diluted solutions the percentage of this hydrolysis is higher. For $\frac{1}{10}$ N potassium-phenolate at 25° the hydrolysis is 3,1 %.[2])

These results are in agreement with the experiments on phenol, which taught that in an alkalic medium phenol practically behaves like a monobasic acid.

In this way the hydrolysis of many of the compositions treated up till now in the above mentioned investigations could be calculated when only enough data were at our disposition with regard to the strength of the respective acids and bases expressed in the well-known units.

---

[1]) H. I. WATERMAN, These Proceedings XX (1917) p. 88, 382, 581.

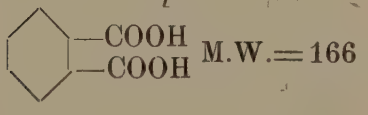
[2]) J. WALKER, Introduction to physical chemistry 1919, p. 330 and 336.

A condition for the calculation is, that the nature of the ions and in general the constitution of the used compositions are known. When this is not the case the method of investigation followed by us may still give some indications. Before applying this method to the investigation of the acid or alkalic properties of organic dyes, we investigated a number of intermediate products. The investigation was also extended over several more or less strongly coloured substances. It was found possible to take away the colour just before the polarimetric measurements by means of norit or of bone-coal without lessening the accuracy of the method. In other cases alcohol was added sometimes. This changed somewhat the nature of the medium, but several compositions that could not be investigated owing to their weak solubility, could now be treated.

Most of the investigated compositions were obtained from KAHLBAUM at Adlershof (near Berlin). When this is not the case it will be mentioned. As further different solutions were primarily coloured we paid little attention to the intensity of the darkening caused by the action of the hydroxylions on the glucose. The obtained analysis numbers will be given here only partly, elsewhere completely.

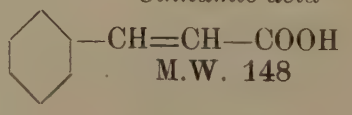
The *naphtyl-amines*. The melting-point of the used α-naphtyl-amine was 50°, that of the β-naphtyl-amine 112°. Hydrochloric compounds of these amines too were used. The experiment in an alkalic medium taught that neither α- nor β-naphtyl-amine bound an alkali, so that they do not influence the decomposition of a glucose in alkalic solution. In hydrochloric solution the amines in question behaved approximately as monovalent bases.

Ortho-phtalic-acid



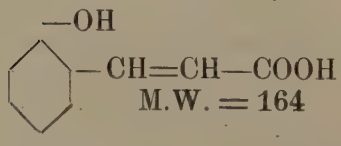
M.W.=166 ,

Cinnamic-acid



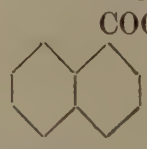
M.W. 148 ,

Ortho-coumaric-acid



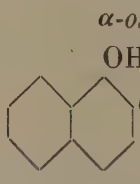
M.W. = 164 ,

α-naphtoic-acid



M.W. = 172

α-oxynaphtoïc-acid



M.W. = 188

The melting-point of the investigated ortho-phalic-acid was 200°,

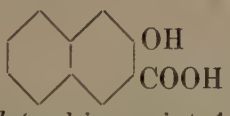
while for this substance is given e. g. 203°; a titration of the acid with $\frac{1}{10}$ N. KOH and phenolphtaleïn as indicator gave the percentage 99,8.

The melting-point of the cinnamic-acid that was present in the laboratory was 133°, of the ortho-coumaric-acid 205°. The α-naphtoïc-acid and the α-oxy-naphtoïc-acid melted respectively at 159° and at 187°.

It was found, that in diluted alcoholic solutions these compounds practically did not hinder the inversion of cane sugar (Table I); Table IV refers to the naphtoïc-acid. From the tables II and III we see, that in alkalic solution the behaviour of ortho-phtalic-acid is dibasic, of α-naphtoïc-acid monobasic, of cinnamic-acid monobasic and finally of coumaric-acid dibasic.

This might have been expected from the above given structural formulae.

We further investigated: *α-naphtol* (M.W. 144, melting-point 96°), *β-naphtol* (M.W. 144, melting-point 122°), 2. 3. oxy-naphtoïc-acid (melting-point 217°)



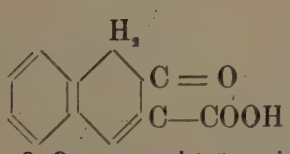
M.W. = 188

and *β-naphtoic-acid* (melting-point 185°, M.W. 172).

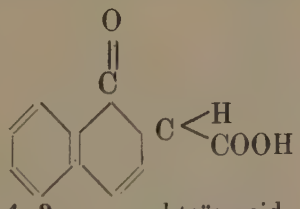
From the experiments made with a nearly 50 %-alcoholic solution we learned, that α- and β-naphtol, α-naphtoïc-acid and 2. 3. oxy-naphtoïc-acid practically do not influence the inversion of cane sugar by hydrochloric-acid (Table IV).

The behaviour of α- and β-naphtol in alkalic solution was approximately monobasic just as of β-naphtoïc-acid; *the* 2.3. *oxynaphtoic-acid behaved in an alkalic medium as a monobasic acid; this was also the case with the* 1. 2. *oxynaphtoic-acid* (Tables V and VI).

In the same way as has been done for the salicylic-acid, led by analogous experiments [1]), we are now inclined to assume also for the mentioned oxynaphtoïc-acids, at least in alkalic media, a "ketoformula", e.g. as follows:



2. 3. oxynaphtoïc-acid
(ketoformula)



1. 2. oxynaphtoïc-acid
(ketoformula)

[1]) H. I. Waterman, These Proc. XX, 581 (1917).

TABLE I.

Influence of α-oxynaphtoïc-acid, cinnamic-acid, ortho-coumaric-acid, ortho-phtalic-acid on the inversion of saccharose by hydrochloric-acid.

		A	B	C	D	E	F	G	H	I	K	Remarks.
		75 cm³ "96 %" technical alcohol										The given time-interval is that of the standing in the thermostat. The readings were made, when the fluids had assumed about the temperature of the polarimeter space. At 35° the α-oxynaphtoïc-acid was just quite dissolved.
added					1162 milligr. phtalic-acid	752 milligr. α-oxynaphtoïc-acid	1036 milligr. cinnamic-acid	656 milligr. o. coumaric-acid				
		50 cm³ of a cane-sugar solution										
Number of cm³ hydrochloric-acid 1,005 N.		0	9	10	10	10	10	10	10	11	12	
		After filling to 150 cm³ placed in the thermostat at a temperature of 35°.										
Polarisation in VENTZKE degrees (tube length 2 dm)	After ± 19 hours	+ 31.0	— 0.4	— 1.3	— 1.9	— 1.5	— 1.5	— 1.5	— 1.5	— 2.3	— 3.3	
	After ± 22½ hours	+ 31.0	— 2.0	— 2.8	— 3.3	— 3.3	— 3.0	— 3.0	— 2.8	— 3.6	— 4.2	
	After ± 41 hours	+ 31.1	— 5.9	— 6.3	— 6.4	— 6.5	— 6.3	— 6.3	— 6.2	— 6.5	—	

TABLE II.

Influence of ortho-phtalic-acid on the decomposition of glucose by an alkali.

		A	B	C	D	E	F	G	H	I	Remarks.
		50 cm³ of a ± 3 % glucose-solution									After addition of the alkali the ortho-phtalic-acid was quite dissolved.
added									581 milligr. o. phtalic-acid		
Number of cm³ potassium hydroxide 0,924 N.		0	2	3	4	5	6	7	10	10	
		Filled to 100 cm³ and placed in the thermostat (33°).									
Polarisation in VENTZKE degrees (2 dm tube)	At the beginning	+ 4.6	+ 4.4	+ 4.2	+ 4.1	+ 4.0	+ 3.9	+ 3.8	+ 4.3	+ 3.7	
	After ± 2¼ hours	+ 4.6	+ 3.3	+ 3.0	+ 2.6	+ 2.4	+ 2.1	+ 1.8	+ 3.2	+ 1.3	
	After ± 3¼ hours	+ 4.6	+ 3.1	+ 2.5	+ 2.2	+ 1.8	+ 1.5	+ 1.2	+ 2.9	+ 0.7	

TABLE III.

Influence of α-naphtoïc-acid, cinnamic-acid and ortho-coumaric-acid on the decomposition of glucose by an alkali.

		A	B	C	D	E	F	G	H	I	Remarks.
		50 cm³ of a ± 3% glucose-solution									By heating the substances were dissolved in the glucose solution. At cooling crystallization took place. By the alkali however all was dissolved again. The solution I was coloured yellowish green after addition of the alkali.
added								344 milligr. α-naphtoïc-acid = 2 m.gr. mol.	1036 milligr. cinnamic-acid = 7 milligr. molecule	328 milligr. cumaric-acid = 2 milligr. molecule	
Number of cm³ potassium-hydroxide 0,929 N.		0	2	3	4	5	10	6	10	6	
		After filling to 100 cm³ placed in the thermostat (36°)									
Polarisation (V. degrees) 2 dm tube	After ± 1½ hours	+ 4.3	+ 3.3	+ 3.0	+ 2.6	+ 2.3	+ 1.4	—	+ 3.1	+ 3.4	
	After ± 3 hours	+ 4.4	+ 2.8	+ 2.3	+ 1.7	+ 1.3	+ 0.5	+ 1.7	+ 2.5	+ 3.0	

TABLE IV.

Influence of α-naphtol, β-naphtol, α-naphtoïc-acid and β-oxynaphtoïc-acid on the inversion of saccharose by hydrochloric-acid.

		A	B	C	D	E	F	G	H	I	K	Remarks.
		75 cm³ "96 %" technical alcohol										The readings were made at room temperature.
dissolved							576 milligr. α-naphtol = 4 milligr. molecules	576 milligr. β-naphtol = 4 milligr. molecules	516 milligr. α-naphtoïc-acid = 3 m.gr. mol.	752 milligr. 2.3oxynaphtoïc-acid = 4 m.gr. mol.		
		50 cm³ cane-sugar solution (concentration 250 Gr./L.)										
Number of cm³ hydrochloric-acid 1,005 N.		0	7	8	9	10	10	10	10	10	10	
		Filled to 150 cm³ and placed in the Thermostat of 35°.										
Polarisation in VENTZKE degrees (2 dm tube)	At the beginning	+ 31.6				+ 31.5	+ 31.5	+ 31.5	+ 31.5	+ 31.5		
	After ± 4 hours	+ 31.5	+ 22.5	+ 21.4	+ 20.3	+ 19.2	+ 18.9	+ 18.5	+ 18.7	+ 18.9	+ 19.2	
	After ± 24 hours	+ 31.5	+ 0.1	— 1.3	— 2.6	— 3.3	— 3.5	— 3.8	— 3.6	— 3.6	— 3.6	
	After ± 28 hours	+ 31.6	— 1.6	— 2.6	— 3.5	— 4.4	— 4.5	— 4.6	— 4.5	— 4.4	— 4.4	
	After ± 50 hours	+ 31.6	— 5.3	— 5.7	— 5.8	— 6.2	— 6.2	— 6.2	— 6.2	— 6.2	— 6.2	

TABLE V.

Influence of β-naphtoïc-acid and β-oxynaphtoïc-acid (2 : 3) on the decomposition of glucose by an alkali.

		A	B	C	D	E	F	G	H	I	K	Remarks.
		50 cm³ of a ± 3 % glucose solution										β-naphtoïc-acid was dissolved in the potassium hydroxide rather quickly, the β-oxynaphtoïc-acid only after long shaking with a yellow colour. The solid acid itself was also yellow.
dissolved									602 milligr. β-naphtoïc-acid = 3,5 m.gr. mol.		1316 m.gr. β-oxynaphtoïc-acid = 7 m.gr. mol.	
Number of cm³ potassium-hydroxide 0,929 N.		0	2	3	4	5	6	7	10	10	10	
		Filled to 100 cm³ and then placed in the thermostat (34°)										
Polarisation in VENTZKE degrees (2 dm tube)	At the beginning	+ 4.4	+ 4.1	+ 3.9	+ 3.8	+ 3.8	+ 3.7	+ 3.7	+ 3.7	+ 3.5	+ 4.0	
	After ± 2¼ hours	+ 4.4	+ 3.2	+ 2.7	+ 2.3	+ 2.1	+ 1.7	+ 1.5	+ 1.6	+ 1.0	+ 3.0	
	After ± 3¼ hours	+ 4.4	+ 2.8	+ 2.3	+ 1.7	+ 1.5	+ 1.1	+ 0.9	+ 1.0	+ 0.3	+ 2.6	

TABLE VI.

Influence of α-oxynaphtoïc-acid (1,2) and β-oxynaphtoïc-acid (2,3) on the decomposition of glucose by an alkali.

		A	B	C	D	E	F	G	H	I	K	Remarks.
		25 cm³ 96 % alcohol										The addition of alcohol was necessary to dissolve the α-oxynaphtoïc-acid.
dissolved									589.6 milligr. 1.2oxynaphtoïc-acid = 0,896.3,5 m.gr. mol.		1179,1 milligr. 2.3 oxynaphtoïc-acid = 0,896.7 m.gr. mol.	
Number of cm³ sodium hydroxide 0,896 N.		0	2	3	4	5	6	7	10	10	10	
		50 cm³ of a glucose solution. After filling to 100 cm³ placed at 35°.										
Polarisation (V. degrees 2 dm tube)	After ± 1½ hours	+ 6.8	+ 5.5	+ 4.8	+ 4.5	+ 4.0	+ 3.6	+ 3.3	+ 3.4	+ 2.4	+ 4.8	
	After ± 4 hours	+ 6.8	+ 4.5	+ 3.6	+ 2.9	+ 2.3	+ 2.0	+ 1.7	+ 1.8	+ 0.9	+ 3.6	
		Further the solutions remained at room temperature.										
	After ± 19 hours	+ 6.8	+ 4.0	+ 3.0	+ 2.4	+ 1.7	+ 1.4	+ 1.1	+ 1.3	+ 0.4	+ 3.1	

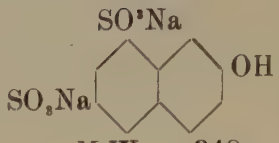
Similar ketoformulae for the 2.3 oxynaphtoïc-acid are already found in the literature [1]).

Further we investigated still :

SCHÄFFER-*salt*,

M.W. = 246

G-salt,



M.W. = 348

and also

sodium p. phenol sulphonate.

M.W. = 196

The sodium 2.6. naphtol sulphonate has been investigated as technical SCHÄFFER-salt and also as a purified one prepared in the laboratory by sulphonation of β-naphtol.

To determine the percentage of the technical product this was titrated by means of diazotated p. nitraniline according to the method in use in the technical control-stations of the dye-manufacturies [2]). In this way we found the percentage 76.4. The purified preparation when dried gave a loss in weight of 11,4 %. In the dried substance we made a sulphate-ash-determination. Having made the calcutation for Na, we found from this 9,1 %. (Theor. 9.35 %).

From the observations combined in table VII we see, that 4 milligram-molecules of the pure SCHÄFFER-salt bind just as much alkali as the corresponding quantity of the technical product.

If the pure salt behaved as a monobasic-acid, just $\frac{88,6}{100} \cdot 4 = 3,5$ cm³ N. KOH would have been found. In reality we find 3,7 cm³ 0,93 N. KOH = 3,4 cm³ N. As the titration gave for the percentage of the technical product 76,4, it is probable, that the technical product in question is made impure by substances which can bind alkali, but which under the circumstances of the titration with diazo-solutions, cannot form colours. As might be expected the SCHÄFFER-salt could not bind an acid in a hydrochloric medium.

---

[1]) R. MÖHLAU, Berichte d. Deutsch Chem. Gesellsch. **28**, 3100 (1895); M. SCHÖPF, Idem **29**, 265 (1896); F. FRIEDL, Sitzungsber. der Akad. der Wissenschaften, Mathematisch-Naturwissensch. Klasse, Wien, **119**, 731(1910).

[2]) R. MÖHLAU and H. BUCHERER, Farbenchemisches Praktikum.

TABLE VII.

Influence of Schäffer-salt (purified) and of Schäffer-salt (technical) on the decomposition of glucose by an alkali.

		A	B	C	D	E	F	G	H	I	K	Remarks.
		50 cm³ of a ± 3 % glucose solution										The substances were dissolved by heating. After cooling the alkali was added. With the potassium-hydroxide the solution H gave a blue fluorescence, while the solution I was coloured brownish green. Before the readings they had to be decoloured by means of norit.
Dissolved									984 milligr. pure sodium SCHÄFFER-salt	984 milligr. technical SCHÄFFER-salt		
Number of cm³ potassium-hydroxide 0,93 N.		0	1	2	3	4	5	6	6	6	6	
		After filling to 100 cm³ placed in the thermostat (temperature 35°).										
Polarisation in V. degrees (tube length 2 dm)	After ± 2¼ hours	+ 4.3	+ 3.7	+ 3.2	+ 2.8	+ 2.4	+ 2.1	+ 1.8	+ 3.1	+ 3.1	+ 1.9	
	After ± 3½ hours	+ 4.3	+ 3.4	+ 2.8	+ 2.2	+ 1.8	+ 1.4	+ 1.0	+ 2.5	+ 2.6	+ 1.0	
		Further left at room temperature.										
	After totally ± 22 hours	+ 4.3	+ 3.2	+ 2.5	+ 1.8	+ 1.4	+ 0.9	+ 0.6	+ 2.3	+ 2.3	+ 0.6	

TABLE VIII.

Influence of sodium para phenol sulphonate (technical) and of G salt (technical) on the decomposition of glucose by an alkali.

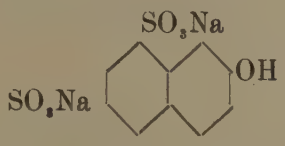
		A	B	C	D	E	F	G	H	I		K		Remarks.
		50 cm³ of a ± 5 % glucose solution												The G-salt is dissolved with a brown colour which makes the readings very difficult. After treatment with norit the fluid is green fluorescent after the filtration, but can be read very well in a 2 dm. tube.
Dissolved									1568 mgr. sodium p. phenol-sulphonate 8 mgr. mol.	2436 mgr. G. salt = 7 milligr. molecules		As sub I		
Added number of cm,³ potassium-hydroxide 092 N.		0	1	2	3	4	5	10	10	10		10		
		After filling to 100 cm³ placed at 35°.												
Polarisation in V. degrees (tube length 2 dm)	After ± 2½ hours	+ 7.4	+ 6.5	+ 5.8	+ 5.2	+ 4.6	+ 4.1	+ 2.3	+ 5.4	norit + 4.4	—	2. 2.2 = + 4.4		
	After ± 4 hours	+ 7.4	+ 6.2	+ 5.2	+ 4.3	+ 3.6	+ 3.0	+ 1.2	+ 4.5	+ 3.6	norit + 3.5	2. 1.8 = + 3.6		
	After ± 5½ hours	+ 7.4	+ 5.8	+ 4.7	+ 3.7	+ 3.0	+ 2.3	+ 0.6	+ 4.0	—	—	norit + 2.9	2.1.5= + 3.0	

The percentage of the sodium 2 . 6 . 8 naphtol disulphonate (*G*-salt) was determined in an analogous way as that of the SCHÄFFER-salt by means of diazotated para-nitraline. The result was 82 %.

For the sodium para phenolsulphonate (technical product) we also found 82 %. The percentage for the dry substance was 87 %. In reality the percentage of sodium in the dry substance (calculated 11,7 %) was 11,3 % (determined with the sulphate-ash method).

The results with *G*-salt and sodium para phenolsulphonate in alkalic solution are to be found in table VIII. From these investigations we see, that 7 milligrammolecules of the technical *G*-salt have bound 6 cm³ KOH (0,92 N.) = 5,5 cm³ N. potassiumhydroxide.

When we suppose that because of the formula



the *G*-salt behaves like a monobasic acid and at the same time that the admixtures, such as the inorganic salts, have no influence and that admixtures as other β-naphtolsulphonates have the same influence as the *G*-salt, we should conclude to a percentage of $\frac{5,5}{7} . 100$ i. e. of nearly 80 % of constituents that can be bound to dyes.

By titration with diazotated paranitroaniline was found 82 %, so that in fact it is nearly sure, that in an alkalic solution the *G*-salt behaves like a monobasic acid.

In an analogous way we may deduce from the observations that in alkalic solution the sodium para phenolsulphonate behaves as a monobasic acid.

Delft, Jan. 1920. *Laboratory of Chemical Technology Delft.*

Physics. — *"Deduction of the dissociation-equilibrium from the theory of quanta and a calculation of the chemical constant based on this."* By Prof. P. EHRENFEST and V. TRKAL.

(Communicated at the meeting of February 28, 1920).

Introduction.

NERNST's theorem, the theory of the specific heat of solids, of the vapour-pressure and of the dissociation-equilibrium must have their common root in the general foundations of statistical mechanics and in the quantum-hypothesis. O. STERN [1]) and H. TETRODE [2]) have shown how from NERNST's theorem by means of EINSTEIN's formula for the specific heat of solids and a vapour-pressure formula for high temperatures (derived kinetically) the chemical constants (hence also the dissociation-equilibrium) may be calculated. Notwithstanding the great advantages of this method a desire must be felt to calculate the chemical constants and the dissociation-equilibrium more directly by considering the hot gases themselves, without the use of a cycle consisting of a condensation, cooling of the crystals to the absolute zero, chemical transformation at $T = 0$, heating of the new crystals and evaporation at the high temperature.

This desire explains the fact, that even after the publication of STERN's paper (1913) attempts have been made again and again to improve the earlier methods of calculating the chemical constants as given by O. SACKUR [3]) in 1911—1913 and H. TETRODE [4]) in 1912. These consist in considering a gas of N equal molecules in a volume V at the temperature T, calculating statistically by means of some formulation of the quantum-hypothesis the "thermodynamic probability W" and by comparing $r \log W$ with the thermodynamic entropy of the gas fixing the indeterminate constant in the entropy. It is not an accident that it is always the same point that remains obscure in these theories [1]), viz, how an expression of the form N^{-N}

[1]) O. STERN, Phys. Ztschr. **14** (1913), p. 629.

[2]) N. TETRODE. Verslag Kon. Ak. v. Wetensch., Amsterdam **23** (II), (1915), p. 1110. Proceedings Amsterdam **17** (1915), p. 1167. [henceforth to be quoted as "IInd paper"].

[3]) O. SACKUR. Ann. d. Phys. **36** (1911), p. 958; **40** (1913), p. 67; Nernst-Festschrift (1912), p. 405.

[4]) H. TETRODE. Ann. d. Phys. **38** (1912), p. 434. [to be quoted as "I st paper"].

(SACKUR) or $(N!)^{-1}$ (TETRODE I) can be forced into the "thermodynamic probability W" in order to obtain an admissible value for the entropy. *The law of dependence on N can only be satisfactorily settled by utilizing a process in which N changes reversibly and then comparing the ratios of the probability with the corresponding differences of entropy.*

If condensation and evaporation (STERN and TETRODE II) are not to be used, and the whole process is to be carried out with gases, it will be necessary to work with a gas-mixture and *change the numbers of molecules $N_1, N_2, \ldots N_j$ of the various gases by dissociation.*

Remembering the real object of the calculation of the chemical constants, viz the deduction of the dissociation-equilibrium, the following formulation of the problem is finally arrived at: Consider $X, Y, Z, \ldots$ atoms of different elements contained in a volume V and possessing an energy E. These atoms can unite to molecules of different kinds in a large number of different ways. *Determine by means of the quantum theory directly, which of the various states of dissociation possesses relatively the greatest probability.*

This problem is to be solved by methods belonging to statistical mechanics and the quantum-theory which will be set forth in § 2 and § 4. On comparing the dissociation-equations arrived at in this manner with the corresponding thermodynamical equations values are obtained for the expressions containing the chemical constants which occur in the latter (§ 6).

Our method removes, as we hope, any remaining obscurities as regards the occurrence of $N_1! N_2! \ldots$. This could only be accomplished, as it appeared to us, by not stopping at the numbers of the *molecules* in the combinatory computations, but by going down to the *atoms*. This is the only way of obtaining a solid common basis for the computation of the relative probability of different states of dissociation (variations of the numbers of molecules N_1, $N_2, \ldots N_j$), viz. the phase-space of $6(X + Y + Z)$ dimensions (§ 4).

The introduction into the combinatory calculation of this refinement, viz. the consideration of the atoms, confirms a result already attained by TETRODE (II): the factor which depends on the permutation of the atoms of the same kind

$$\frac{X!\,Y!\,Z!}{N_1!\,N_2!\ldots N_j!\;\sigma_1^{N_1}\sigma_2^{N_2}\ldots\sigma_j^{N_j}} \quad \text{(comp. e.g. (18)}$$

[1]) Comp. § 9.
[2]) Comp. § 8.

contains not only the expression $N_1! \; N_2! \; . \; . \; . \; N_j!$, but also the "symmetry-numbers" of the molecules $\sigma_1, \; \sigma_2, \; . \; . \; . \; , \sigma_j$ (comp. e.g. (6) § 3). These, therefore, influence the dissociation-equilibrium (comp. § 8).

Accordingly the numerical value of the chemical constant of a molecule should depend not only on its mass and moment of inertia, but also on the "symmetry-number" of the molecule.

The question whether any of the cases of dissociation-equilibrium or evaporation which have been investigated numerically, speak in favour of or against this modification, we shall leave to others who are more familiar with the experimental side of the question.

§ 1. Fully excited and non-excited degrees of freedom.

The *thermodynamic* theory of the dissociation-equilibrium considers the molecules as having *constant specific heats* in the range in question, i.e. possible changes of the specific heats are left out of account in the calculations. If they were taken into account, the expressions for the entropy and energy of the gasmixture would not have the special form, which is essential for the definition of the "chemical constant" [1]).

In a kinetical theory of the dissociation-equilibrium analogous assumptions or approximations must therefore be admitted, if a kinetic interpretation of the chemical constant is aimed at.

We shall make the following assumption in our calculations:

I. The translational motions of the molecules as also their rotations [2]) (with the exception of those referred to under II) will be considered entirely free from any limitations depending upon quanta [3]) ("fully excited degrees of freedom").

II. On the other hand the following motions will be assumed to be absent [4]) ("non-excited degrees of freedom):

a. The rotation of di-atomic molecules about the axis of symmetry and all rotation of mon-atomic molecules.

---

[1]) Compare the expressions for the energy and entropy in § 5 and in M. PLANCK, Thermodynamik §§ 237 — 241.

[2]) We therefore exclude for the special object of our theory these cases, in which a rotation happens to be in the intermediate state of being "partially excited", as these would introduce a variable specific heat (Comp. NERNST. Theor. u. exp. Grundlagen d. neuen Wärmesatzes, p. 136 bottom p. 137 top).

[3]) i.e. we approximate for these degrees of freedom all summations over successive quanta-steps by the corresponding $\int\int dq \; dp$; comp. "addit notes 1".

[4]) i.e. for these degrees of freedom we confine ourselves in our calculation of the sum to the lowest quantum-stage.

b. Internal motions of the atoms in the molecule [1]).

Note. In accordance with PLANCK's first quantum-theory we have provisionally assumed the lowest quantum-grade to be that of no quanta. N. BOHR's investigations (On the Quantum Theory of line-spectra (Part II), D. Kgl. Danske Vidensk. Selsk. Skrifter, Naturvidensk. og mathem. Afd., 8. Raekke N. 1, København, 1918) show, that probably in many cases the stage with the quantum-number 1 must be taken as the lowest possible. The corresponding modifications might easily be introduced in the theory (and also specially the contribution of the kinetic side by side with the potential energy).

§ 2. The phase-space of a molecule (μ-space). The μ-weight $\{\mu\}$.

If a molecule consists of ξ, η, ζ atoms of say three different chemical elements, its "phase" may be determined by means of $6(\xi + \eta + \zeta)$ cartesian co-ordinates and momenta, i. e. by a point in a $6(\xi + \eta + \zeta)$-dimensional "μ-space" (phase-space of the molecule). In consequence of the assumptions II*a* and II*b* of the previous section, however, as long as the molecule is not dissociated, its phase-point ("μ-point") is confined to a portion of the μ-space, namely to a 2×6, 2×5 or 2×3-dimensional region according as the molecule is poly-atomic, di-atomic or monatomic.

Considering for a moment the case of a poly-atomic molecule ($\xi + \eta + \zeta$ atoms), this sub-space may be described af follows: owing to the rigidity of the molecule the $3(\xi + \eta + \zeta)$ cartesian co-ordinates of the atoms may be expressed by 6 co-ordinates $q_1, q_2, \ldots q_6$, which fix the position and orientation of the molecule. Similarly the cartesian momenta are determined by the six momenta $p_1, p_2, \ldots p_6$ corresponding to the $q_1 \ldots q_6$. If in accordance with assumption I of the previous section we imagine the quantities $q_1 \ldots p_6$ to vary continuously within any arbitrary limits, the "μ-point" describes inside the $6(\xi + \eta + \zeta)$ dimensional μ-space a

[1]) This assumption underlies so far all derivations of the chemical constants for di-or monatomic molecules; for the theories never go beyond „rigid" molecules. This assumption seems more extra-ordinary in the present theory, in which the dissociation of the molecules is directly considered. Indeed, the molecules must first be gradually loosened, before they can dissociate. Still our method of calculating agrees with the following assumption: either every internal degree of freedom of the molecule is on its lowest quantum-grade, or the molecule is completely dissociated. This is of course only meant as an approximation in the calculation, similar to what is done in the thermodynamic derivations, where the variable contribution to the specific heat is neglected which would be due to a loosening of the molecules.

portion of a "surface" of 12 dimensions and the quantities $q_1 \ldots p_6$ play the part of curvilinear parameters on this surface.

We define[1]) the following expression as the "μ-weight" $\{\mu\}$ of this region:

$$\{\mu\} = h^{3(\xi+\eta+\zeta)-6} \cdot \int \ldots \int dq_1 \ldots dq_6\, dp_1 \ldots dp_6, \quad \ldots \quad (1)$$

where the integration is to be extended over the region in question.

In future applications (§ 4) the molecule will have to pass through the total volume V of a vessel and similarly through all possible orientations. Accordingly, integrating with respect to the co-ordinates q, we have

$$\{\mu\} = h^{3(\xi+\eta+\zeta)-6} \cdot V \cdot 4\pi \cdot 2\pi \cdot \int \ldots \int dp_1 \ldots dp_6 \quad \ldots \quad (2)$$

The corresponding expressions for di- and mon-atomic molecules are as follows

$$\{\mu\} = h^{3(\xi+\eta+\zeta)-5} \cdot V \cdot 4\pi \cdot \int \ldots \int dp_1 \ldots dp_5, \quad \ldots \quad (3)$$

$$\{\mu\} = h^{3(\xi+\eta+\zeta)-3} \cdot V \cdot \int \ldots \int dp_1 \ldots dp_3 \quad \ldots \quad (4)$$

In (3) $\xi + \eta + \zeta = 2$ and in (4) $= 1$, but we have left the power of h in its above form in order to obtain the formulae in our calculations later on as symmetrical as possible (§ 4).

§ 3. The constitution of the gas-mixture.

In a vessel of volume V X, Y, Z atoms of say 3 different chemical elements (atomic masses m_ξ, m_η, m_ζ) may be introduced. These molecules can associate to molecules in a number of different ways. At a special moment let there be present j different kinds of molecules; a molecule of the kind i may consist of ξ_i, η_i, ζ_i atoms and may possess the following mass, moments of inertia and potential energy respectively:

$$M_i;\ P_i, Q_i, R_i;\ \chi_i \quad \ldots \quad (5)$$

The arbitrary constant contained in χ_i, we shall fix by the following rule: we shall ascribe to the atoms a potential energy 0, when they are completely separated from each other; χ_i is therefore a *negative* quantity, viz. equal to the negative work which the atoms give off, in uniting to form the molecule.

It may happen that, owing to the special distribution of similar atoms in a molecule, the latter possesses more than one completely

[1]) Comp. the illustration of this definition by means of a special simple case n addit. notes I.

equivalent rotational orientation; its number may be called the

Symmetry-number σ_i . . . . . (6)

of the molecule. (For instance for J_2 σ would be $= 2$, for CH_4 (methane) $\sigma = 12$).

Finally we shall call f_i the number of fully-excited degrees of freedom of the molecule; therefore

$$f_i = 3, 5, 6 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

according as the molecule in question contains one, two or more atoms.

The numbers of the molecules of different kinds $N_1, N_2, \ldots . N_j$, have to satisfy the equations

$$\sum_1^j N_i \xi_i = X, \quad \sum_1^j N_i \eta_i = Y, \quad \sum_1^j N_i \zeta_i = Z, \quad . \quad . \quad . \quad (8)$$

i.e. with varying degree of dissociation the numbers $N_1 \ldots N_j$ change, as also the total number of molecules

$$N = \sum_1^j N_i \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

but not the numbers of the atoms.

The total energy of the gas-mixture is given by the equation

$$E = K + \Sigma N_i \chi_i, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

where K stands for the total kinetic energy of all the molecules.

In the thermodynamic calculation of the dissociation-equilibrium (§ 6) we shall use "molar" instead of molecular quantities. Calling AVOGRADO's number

$$\mathfrak{N} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

we have the following relations for the number of gram-molecules n_i, for the potential and kinetic energies pro gram-molecule (b_i, C_i, T) and for the specific heat (C_i) respectively

$$n = \frac{N_i}{\mathfrak{N}}, \quad b_i = \mathfrak{N}\chi_i, \quad C_i\, T = \mathfrak{N} \,.\, f_i \, \frac{rT}{2}, \quad C_i = \mathfrak{N} \frac{f_i}{2} r \quad . \quad (12)$$

where

$$r = \frac{R}{\mathfrak{N}}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (13)$$

hence

$$n_i R = N_i r. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (14)$$

§ 4. The phase-space of the gas (γ-space). The γ-weight $\{\gamma\}$.

The most general "phase" of our system may be represented by the 6 $(X + Y + Z)$ cartesian co-ordinates and momenta of the

$X+Y+Z$) atoms, and therefore by a "γ-point" in a $6(X+Y+Z)$-dimensional "γ-space". To a given condition of dissociation $(N_1, N_2 \ldots N_j)$ of the gas-mixture, owing to the assumptions II (§ 1), a sub-space corresponds of $2F$ dimensions, where

$$F = \sum_1^j N_i f_i; \quad \ldots \ldots \ldots \quad (15)$$

f_i as before being equal to 3, 5, or 6 according as the index i refers to molecules of one, two or more atoms (comp. eq (7).

We must now consider more in detail the structure of this sub-space.

Consider an individual "phase" of the system (any point γ_1 of the γ-space); the $X+Y+Z$ atoms, which we shall provisionally think of as being individualized by numbers attached to them, are associated to N molecules, which we shall also suppose to be individually numbered. The total energy of the system then also possesses a definite value E. We now apply to the phase of the system changes of two types (A) and (B) [1]), which both leave the dissociation $(N_1, N_2, \ldots, N_j)$ and the total energy unchanged.

Changes of type [A]. Starting from the initial phase γ_1 we make the molecules independently of each other, pass through the total volume V [2]) and all possible rotational orientations, and also make them assume successively all possible velocities of translation and rotation, *which are in accordance with the original total energy.*

While in this manner the γ-point starting from γ_1 describes a region (A_1) of the γ space, the μ-points of the various individual molecules — each in its own μ-space — describe the regions which were discussed in § 2. In the classical theory the "γ-volume" is obtained in cases of this kind by taking the product of the corresponding "μ-volumes". Analogously we shall here *define* the γ-weight $\{\gamma\}_{(A_1)}$ of the region just mentioned by the relation

$$\{\gamma\}_{(A_1)} = \prod_1^j \{\mu_i\}^{N_i} \quad \ldots \ldots \ldots \quad (16)$$

where for $\{\mu_i\}$ we have to take the expressions (4), (3), or (2) of § 2 according to whether i corresponds to a molecule of one, two or more atoms. The limits of the integrations over the momenta occurring in (16) are determined by the fact, that on account of

---

[1]) Comp. the somewhat similar discussion in P. and T. EHRENFEST, Math. Enc. Bd. IV. Art. 32, § 12 *b*.

[2]) The volume-correction which is due to the finite dimensions of the molecules is left out of account.

the prescribed total energy E and dissociation $N_1, N_2, \ldots N_j$ the total kinetic energy

$$K = E - \Sigma N_i \chi_i \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (17)$$

is also fixed (comp. (10) in § 3 and the computations further on in § 6.

Changes of type [B]. By the mutual permutations of *similar*-atoms starting from a given γ-point new γ-points arise [1]). In connection with the $X!Y!Z!$ possible permutations of the individual atoms of the same kind a set of $X!Y!Z!$ different γ-points in the γ-space will be seen to belong together and all these points give the gas the same E and the same dissociation $(N_1, N_2, \ldots)$.

In order to reach the *total* γ-region which agrees with γ, in the quantities N and $N_1, N_2, \ldots N_j$ we must combine the changes of the two types $[A]$ and $[B]$, in such a manner, however, that *no portion of the region is counted twice.*

It may be proved, that including the region (A_1) altogether Ψ identical regions (A_1), (A_2), $\ldots A\Psi$, are obtained, in this manner, where

$$\Psi = \frac{X!\,Y!\,Z!}{N_1!\,N_2! \ldots N_j!\,\sigma_1^{N_1}\sigma_2^{N_2}\ldots\sigma_j^{N_j}} \quad . \quad . \quad . \quad (18)\ ^2)$$

We shall give a few short indications as regards the proof of this statement. For this purpose we introduce the notion of "internal" permutation.

A permutation of the atoms will be called internal, if the result may also be obtained by translations and rotations of the *rigid* molecules.

Simple instances. 1. Two molecules of the same kind are made to exchange their position and orientation by translation and rotation. 2. A molecule of symmetry-number σ_i^* (comp. eq. (6)) is made to pass from one orientation to another equivalent one [3]). 3. The same operations are carried out at the same time with a number of molecules.

An internal permutation carries the phase-point of the system say from γ' to γ''; but here the following circumstance must be remembered: γ' is still inside

---

[1]) Since each individual atom has six co-ordinate axes of the γ space referring to it. Thus when two atoms of the system are exchanged, nearly all co-ordinates of the γ point remain unchanged, only 12 co-ordinates exchanging their values two by two.

[2]) BOLTZMANN in his well-known paper: "Ueber das Arbeitsquantum, welches bei chemischen Verbindungen gewonnen werden kann," [Wied. Ann. **22** (1884), p. 39. Wisschensch, Abh. III, p. 71] has determined a similar combinatory quantity. But in comparing the quantity Z in his equation (3) with our , the difference should be noted which is referred to in the next note 3.

[3]) In a molecule of the constitution ABA, therefore, the permutation of the two A atoms is an internal one, in a molecule of the form AAB it is not. With BOLTZMANN the latter permutation would also have to be regarded as internal. This difference is due to the fact that with him the changes of type $[A]$ form a wider class than with us and contain all exchanges of similar atoms inside the same molecule.

the phase-region (A'), which is formed from γ' by the changes of type $[A]$ A [1]) (that is what the word "internal" is meant to express).

Taking any phase-point γ as starting point, there are always

$$\mathfrak{D} = N_1!\, N_2! \ldots N_j!\, \sigma_1^{N_1} \sigma_2^{N_2} \ldots \sigma^{Nj} \quad . \quad . \quad . \quad . \quad (19)$$

internal permutations [2]) and all γ-points reached in that way lie inside one and the same A-region.

It will therefore be clear, that, if from the original phase γ_1 by an operation $[A]$ we produce the phase-region A_1, and if we then apply the $X!\ Y!\ Z!$ operations of type $[B]$ to every point of the region (A_1), we do not obtain $X!\ Y!\ Z!$ regions similar to (A_1), but altogether only Ψ (eq. (18)), since the $X!Y!Z!$ permutations of the atoms divide into Ψ groups of $\mathfrak{D}$. internal permutations each.

Combining (16) and (18) we obtain for the total γ-weight of *all* the phases, which belong to given values of V, E and N_1, $N_2 \ldots N_j$ the expression:

$$\{\gamma\} = \frac{X!\ Y!\ Z!}{N_1!\, N_2! \ldots N_j!\, \sigma_1^{N_1} \sigma_2^{N_2} \ldots \sigma_j^{N_j}} \{\mu_1\}^{N_1} \{\mu_2\}^{N_2} \ldots \{\mu_j\}^{N_j} \quad . \quad (20)$$

The expressions $\{\mu_i\}$ contain the integrals with respect to the momenta of all possible motions of translation and rotation of the molecules which have still to be computed.

The total kinetic energy of the molecules is fixed by equation (17); the integration is to be taken over all the values of the momenta which are compatible with it. Calling these momenta for a moment $p_1, p_2 \ldots p_F$, F being given by equation (15), we have the following relation between these quantities:

$$\frac{p_1^2}{2A_1} + \frac{p_2^2}{2A_2} + \ldots + \frac{p_F^2}{2A_F} = K, \quad . \quad . \quad . \quad . \quad . \quad (21)$$

where $A_1, A_2, \ldots, A_F$ represent the various molecular masses or moments of inertia

$$M_1, P_1, Q_1, R_1; \ . \ . \ . \ . \ ; M_j, P_j, Q_j, R_j, \quad . \quad . \quad . \quad . \quad (22)$$

according to the index (comp. (5) in § 3).

The multiple integrals with respect to the momenta give together the surface of the "ellipsoid" (21). Neglecting numbers of the order 1 as compared with the large number F, we may use for it the following approximation [3]).

---

[1]) For the operations $[A]$ include all possible translations and rotations of the molecules, hence also those, which may replace our *internal* permutations

[2]) The centres of gravity of the N_i molecules of type i may mutually exchange their N_i positions and moreover each of these molecules can choose among the σ_i equivalent orientations.

[3]) The volume I of a sphere of radius R in a space of F dimensions and its

$$\frac{1}{\Gamma\left(\frac{F}{2}\right)}(\sqrt{2K\pi})^F \sqrt{A_1 A_2 \ldots A_F} \quad \ldots \ldots \quad (23)$$

If we now include the remaining factor in the expressions $\{\mu_i\}$ (comp. eq. (2), (3), (4) in § 2), having regard to the meaning of the quantities A_1, $A_2, \ldots, A_F$, the expression (20) for $\{\gamma\}$ becomes as follows:

$$\left.\begin{aligned}\{\gamma\} = \frac{X!\,X!\,Z!}{N_1!\,N_2! \ldots N_j!\,\sigma_1^{N_1}\sigma_2^{N_2}\ldots\sigma_j^{N_j}} \cdot h^{3(X+Y+Z)}\, V^N \cdot \frac{1}{\Gamma\left(\frac{F}{2}\right)} \cdot \\ \cdot (\sqrt{2K\pi})^F \cdot \prod_1^j (\alpha_i'' h^{-f_i})^{N_i},\end{aligned}\right\} \quad (24)$$

where

$$\left.\begin{aligned}\alpha_i'' &= 4\pi \cdot 2\pi \sqrt{M_i^3 P_i Q_i R_i} && \text{for poly-atomic molecules} \\ \alpha_i'' &= 4\pi \quad \sqrt{M_i^3 P_i^3} && \text{,, di- ,, ,,} \\ \alpha_i'' &= \quad \sqrt{M_i^3} && \text{,, mon- ,, ,,}\end{aligned}\right\} \quad (25)$$

the quantities f_i, F and N being defined by equations (7) § 3, (15) § 4 and (9) § 3.

§ 5. log $\{\gamma\}$ and the entropy for an arbitrary degree of dissociation $(N_1, N_2 \ldots, N_j)$.

Using STIRLING's formula log $\{\gamma\}$ assumes the following approximate form

$$\log\{\gamma\} = I + N \log V + \frac{F}{2}\log K + F \log\sqrt{2\pi} + \Sigma N_i (\log\alpha_i'' - f_i \log h - \log\sigma_i)$$

$$- \Sigma N_i (\log N_i - 1) - \frac{F}{2}\left(\log\frac{F}{2} - 1\right) \quad \ldots \quad (26)$$

or

---

surface O (i.e. the differential coefficient of I with respect to R) are respectively [comp. say P. H. SCHOUTE, Mehr-dimensionale Geometrie, Bd. II, (Sammlung Schubert, Leipzig 1905); J. H. JEANS, The Dynamical Theory of Gases, § 46]:

$$J = \frac{1}{\Gamma\left(\frac{F}{2}+1\right)}\sqrt{\pi}^F R^F, \quad O = \frac{1}{\Gamma\left(\frac{F}{2}\right)}\sqrt{\pi}^F R^{F-1}.$$

It is in accordance with the usual approximations of the kinetic theory (F very large as compared with 1), if we put $\log J$ and $\log O$ equal to each other, since for instance, if we use STIRLING's approximation, expressions are obtained for these quantities, which coincide completely, if we do not make any difference between F and $F-1$. We have used a similar approximation with regard to the ellipsoïd.

$$\log\{\gamma\} = I + \Sigma N_i \left[\log V + \frac{f_i}{2} \log K + \log \alpha_i' \right]$$

$$- \Sigma N_i [\log N_i - 1] - \frac{F}{2} \left[\log \frac{F}{2} - 1 \right], \quad . \quad . \quad . \quad (27)$$

where

$$I = \log [X!\, Y!\, Z!\, h^{3(X+Y+Z)}], \quad . \quad . \quad . \quad . \quad (28)\ ^{1})$$

$$\log \alpha_i' = \log \alpha_i'' - f_i \log h - \log \sigma_i + f_i \log \sqrt{2\pi} \quad . \quad . \quad . \quad (29)$$

therefore

$$\alpha_i' = \frac{\alpha_i''}{\sigma_i} \left[\frac{\sqrt{2\pi}}{h} \right]^{f_i} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (30)$$

If there are $n_1, n_2, \ldots, n_j$ gram-molecules of ideal gases of different kinds in the volume V at the temperature T, the entropy and energy of the mixture are given by the expressions:

$$\left.\begin{aligned} S &= \Omega + \Sigma n_i \left(R \log \frac{V}{n_i} + C_i \log T + \varkappa_i \right) = \\ &= \Omega + \Sigma n_i \left(R \log V + C_i \log T + \varkappa_i \right) - R \Sigma n_i \log n_i \end{aligned}\right\} \quad . \quad (31)$$

$$E = \Sigma n_i (C_i T + b_i) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (32)$$

Ω is a quantity which is independent of V, T and the numbers n_i, but may depend on the numbers of gram-atoms of the different kinds of *atoms* in the system (say x, y, z) [2]), b_i is the potential energy of a molecule of the kind i as compared with the condition of complete dissociation, which is taken as the zero of potential energy, and C_i the specific heat at constant volume.

§ 6. Comparison of the kinetic and the thermodynamic calculations of the dissociation-equilibrium. The resulting values of the chemical constants.

We now introduce the following axiom: *With given numbers of atoms X, Y, Z, volume V and total energy E the dissociation-equilibrium is characterized by these values of the numbers of molecules* $N_1, N_2, \ldots, N_j$, *for which* $\log\{\gamma\}$ *is a maximum.*

---

[1]) It may be noted, that, when all the numbers of atoms and molecules, the volume V and the total kinetic energy are doubled, the numerical values of $\log \frac{V}{N}$ $\log \frac{K}{F}$ in the expression for $\{\gamma\}$ remain the same and the value of the sums is therefore also doubled, whereas I increases to more than twice its value on account of $X!\ Y!\ Z!$ Comp. § 9.

[2]) In the theory as usually given (comp. say M. PLANCK, Thermo-dynamik. 4 Aufl. § 237) Ω is left out. Incomparing the entropy with the "logarithm of the probability" this becomes the source of great obscurity (comp § 9).

Let

$$\delta N_i = \nu_i \delta Q \quad \text{or} \quad \delta n_i = \nu_i \delta q \quad . \quad . \quad . \quad . \quad (33)$$

represent any possible [1]) chemical reaction in the system, i. e. a reaction which is compatible with the given numbers of atoms X, Y, Z; $\nu_1, \nu_2, \ldots, \nu_j$ are certain positive or negative whole numbers, which give the numbers of the molecules which are formed or disappear in the elementary reaction [2]).

The kinetic and thermodynamic deductions of the dissociation-equilibrium may now be given side by side:

(kinetic)	(thermodynamic)
$\delta \log\{\gamma\} = 0 \quad . \quad . \quad (34)$	$\delta S = 0 \quad . \quad . \quad . \quad (34')$
$\delta V = 0, \quad \delta N_i = \nu_i \delta Q \quad . \quad (35)$	$\delta V = 0, \quad \delta n_i = \nu_i \delta q \quad . \quad (35')$
$\delta E = \delta(K + \Sigma N_i \chi_i) = 0 \quad (36)$	$\delta E = \delta \Sigma n_i (C_i T + b_i) = 0 \quad (36')$

Substitution of the expressions (26), (31) § 5 for $\log(\gamma)$ and S and further development of the maximum-problems lead to

$\Sigma \nu_i \log N_i = (\log V) \Sigma \nu_i + \Sigma \nu_i \log \alpha_i'$	$\Sigma \nu_i \log n_i = (\log V) \Sigma \nu_i + \frac{1}{R} \Sigma \nu_i (\varkappa_i - C_i - R)$
$-\frac{F}{2K} \Sigma \nu_i \chi_i + \left(\log \frac{2K}{F}\right) \Sigma \nu_i \frac{f_i}{2} \quad (37)$	$-\frac{1}{RT} \Sigma \nu_i b_i + (\log T) \cdot \frac{1}{R} \Sigma \nu_i C_i \quad (37')$

In (37') we shall express V in the pressure p of the gas-mixture by means of the equation

$$pV = RT \Sigma n_i \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (38)$$

Further in (37) we shall put

$$K = F \cdot \frac{rT}{2}, \qquad pV = rT \Sigma N_i \quad . \quad . \quad . \quad . \quad (39)$$ [3])

---

[1]) In general more than one reaction is possible between the molecules of the mixture each characterized by a special set of values of the numbers $\nu_1, \nu_2, \ldots, \nu_j$.

In order to establish the dissociation-equilibrium completely, and to obtain the necessary number of equations between the equilibrium concentrations, all the different reactions [variations] have to be taken in succession [Comp. M. PLANCK, Thermodynamik § 247].

[2]) M. PLANCK, Thermodynamik § 244.

[3]) Properly speaking these two equations must be taken as giving *definitions* of the quantities p and T: the phase-region in the "γ-space" which corresponds to the prescribed values of V, E and $N_1, N_2, \ldots N_j$ contains beside MAXWELL-BOLTZMANN states, others which deviate strongly from those and for which therefore in themselves the conceptions of "pressure and temperature of the gas" have no meaning at all. However, the very great majority of the phase-points of this region are of the MAXWELL-BOLTZMANN type of distribution or closely resembling ones, and for those the relations (39) hold with the ordinary meaning of the quantities p and T.

and instead of the numbers $N_i, (n_i)$ we shall introduce the "concentrations"

$$c_i = \frac{N_i}{N_1 + N_2 + \ldots + N_j} = \frac{n_i}{n_1 + n_2 + \ldots + n_j} \quad . \quad . \quad (40)$$

This gives

$$\left.\begin{aligned} &\Sigma\, \nu_i \log c_i = -(\log p)\, \Sigma\, \nu_i \\ &+ \Sigma\, \nu_i \log \alpha_i' - \frac{1}{rT} \Sigma\, \nu_i \chi_i \\ &+ (\log rT)\, \Sigma\, \nu_i \left(\frac{f_i}{2} + 1\right) \end{aligned}\right\} (41) \qquad \left.\begin{aligned} &\Sigma\, \nu_i \log c_i = -(\log p)\, \Sigma\, \nu_i \\ &+ \frac{1}{R} \Sigma\, \nu_i (\varkappa_i + R \log R - C_i - R) \\ &- \frac{1}{RT} \Sigma \nu_i b_i + (\log T) \frac{1}{R} \Sigma \nu_i (C_i + R) \end{aligned}\right\} (41')$$

On comparing (41') with (41) and in view of (12) to (14) § 3, we obtain for the "chemical constants"

$$\alpha_i = \varkappa_i + R \log R - C_i - R \quad . \quad . \quad . \quad . \quad . \quad . \quad (42)$$

following equation

$$\frac{1}{R} \Sigma\, \nu_i \alpha^i = \Sigma\, \nu_i \left\{ \log \alpha_i' + \left(\frac{f_i}{2} + 1\right) \log r \right\} . \quad . \quad . \quad (43)\ ^1)$$

or

$$\frac{1}{R} \Sigma\, \nu_i \alpha_i = \Sigma\, \nu_i \alpha_i \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (44)$$

where

$$\alpha_i = \log \alpha_i' + \left(\frac{f}{2} + 1\right) \log r \quad . \quad . \quad . \quad . \quad . \quad (45)$$

hence by (30) and (25)

$$\left.\begin{aligned} \alpha_i &= \log \left[\frac{4\pi \,.\, 2\pi}{\sigma_i} \sqrt{M_i^3\, P_i\, Q_i\, R_i} \left(\frac{\sqrt{2\pi r}}{h}\right)^6 r \right] \\ \alpha_i &= \log \left[\frac{4\pi}{\sigma_i} \sqrt{M_i^3\, P_i^2} \left(\frac{\sqrt{2\pi r}}{h}\right)^5 r \right] \\ \alpha &= \log \left[\sqrt{M_i^3} \left(\frac{\sqrt{2\pi r}}{h}\right)^3 r \right] \end{aligned}\right\} . \quad . \quad . \quad (46)$$

for poly-atomic, di-atomic and mon-atomic molecules respectively.

§ 7. Remarks on additional contributions of the atoms to the chemical constant of the molecule which remain indeterminate.

Molecules of the kind as considered here may undergo a large number of different chemical reactions, each characterized by a

---

[1]) The term with $\log r$ is derived from $\log r\ T$ in equation (41).

different set of numbers $\nu_1, \nu_2, \ldots, \nu_j$ [1]). Each time we obtain a corresponding equation for the chemical constants of these molecules

$$\frac{1}{R} \Sigma \nu_i a_i = \Sigma \nu_i \alpha_i \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (47)$$

It will be seen, however, that the quantities a_i are not completely determined by these relations. For *every* chemical reaction which is possible the corresponding numbers $\nu_1, \nu_2, \ldots, \nu_j$ have to satisfy the relations:

$$\Sigma \nu_i \xi_i = 0, \qquad \Sigma \nu_i \eta_i = 0, \qquad \Sigma \nu_i \zeta_i = 0 \quad . \quad . \quad . \quad (48)$$

Therefore: for every chemical reaction the corresponding equation (47) will be satisfied by putting

$$\frac{a_i}{R} = \alpha_i + \xi_i u + \eta_i v + \zeta_i w . \quad . \quad . \quad . \quad . \quad . \quad (49)$$

with *completely arbitrary values* of the numbers u, v, w, that is to say: *the chemical constant of a molecule is completely determined but for certain additive constants, which the several atoms bring with them into the molecule and carry away, with them in chemical reactions* [2]). In the determination of the dissociation-equilibrium these arbitrary constants drop out, since in that case, as we have seen, we only deal with $\Sigma \nu_i a_i$.

§ 8. The influence on the dissociation-equilibrium of the "symmetry-numbers" σ_i of the molecules.

The part played by the symmetry-numbers in the dissociation-equilibrium may be elucidated by a typical example.

Let the chemical elements A and B be able to form the following kinds of molecules

[1]) Comp. not 1 in § 6.

[2]) Obviously the entropy-constants K_i have exactly the same degree of determinateness and indeterminateness. The same indeterminateness remains, when the chemical constants are derived by means of the vapour-pressure equation (comp. "additional notes" III), and also, if following BOLTZMANN one would make use of the equation

$$S^* - S = r \left[log \{\gamma^*\} - log \{\gamma\} \right]$$

For also the numbers of molecules N_1^* N_2^*, . . . N_i^* and N_1, N_2, . . . N_i occurring in this equation have again to satisfy relations of the form.

$$N_i^* - N_i = \nu_i \Delta Q \qquad \text{(comp. (33) § 6).}$$

in order that the change may be compatible with the number of atoms X, Y, Z, present. We do not think that BOLTZMANN's equation can be replaced by an assumption of the form.

$$S = r \, log \{\gamma\}$$

on grounds which will be set forth in § 9.

$$A, \quad B, \quad AAB, \quad ABA, \ldots \ldots \quad (50)$$

the concentrations, moments of inertia, potential-energies and symmetry-numbers being as follows

$$\left.\begin{array}{cccc} c_1 & c_2 & c_3 & c_4 \\ 0 & 0 & P_3 & P_4 \\ 0 & 0 & \chi_3 & \chi_4 \\ 1 & 1 & 1 & 2 \end{array}\right\} \ldots \ldots \quad (51)$$

The two reactions

$$AAB \rightleftarrows A + B \text{ and } ABA \rightleftarrows A + B, \ldots \quad (52)$$

give dissociation-equations of the following form

$$\frac{c_3}{c_1^2 c_2} = G P_3 e^{-\frac{\chi_3}{rT}} \qquad \frac{c_4}{c_1^2 c_2} = \tfrac{1}{2} G P_4 e^{-\frac{\chi_3}{rT}}. \ldots \quad (53)$$

since all the quantities are the same in the two cases with the exception of $P_3 \neq P_4$, $\chi_3 \neq \chi_4$ and $\sigma_3 \neq \sigma_4$. (G is supposed to contain the quantities which are common to the two cases).

If therefore for instance approximately $P_3 = P_4$ and $\chi_3 = \chi_4$, we should have

$$\frac{c_3}{c_4} = 2, \ldots \ldots \quad (54)$$

or *the concentration of the unsymmetrical molecules is about twice that of the symmetrical molecules.*

§ 9. Critical remarks on some allied deductions of the chemical constants.

Whereas Boltzmann in his theory uses the equation

$$S_2 - S_1 = r \log \frac{W_2}{W_1} \ldots \ldots \quad (59)$$

throughout, Planck and many others following him replace it by the relation

$$S = r \log W. \ldots \ldots \quad (60)$$

It was obviously Nernst's theorem that first started this preference of (60) over (59), as on the one hand it provided a natural zero-condition for the calculation of S and on the other a natural common unit for the estimation of W, viz. any condition of the system at $T = 0$.

In the majority of calculations of the chemical constants a special obscurity remains as to the way in which the "thermodynamic probability" of a gas depends on the number of molecules.

We shall try to explain in a few words, how this obscurity is

connected with the use of equation (60) [1]: it is generally assumed as self-evident, that the entropy of a gas is to be taken twice as large, if the number of molecules and the volume are both doubled. Now it is certainly true, that the *increase* of the entropy in a given process in a gas of twice the number of molecules is twice as large as the corresponding increase in the original gas. But what is the meaning of taking the *entropy itself* twice as large and *thereby settling the entropy-difference between the doubled and the original gas?* By what reversible process is the double quantity of gas to be generated from the original quantity? Without that the entropy-difference $\int \frac{dQ}{T}$ cannot be clearly defined. On account of equation (60) one is then confronted with the difficult problem of choosing the definitions in such a manner that the "thermodynamic probability, of the double quantity of a gas is equal to the square of the "thermodynamic probability of the single quantity. [2])

In order to remove this obscurity it is necessary to return to BOLTZMANN's equation (59) and to apply it to a reversible process in which the numbers of the molecules change.

We shall now go a little more fully into the relation in which our theory stands to others which are closely allied to it. [3]) Special interest attaches to the manner, in which in the various theories the terms $N_i \log N$ are produced. In our theory they originate in the combinatory factor:

$$\mathfrak{P} = \frac{X!\, Y!\, Z!}{N_1!\, N_2! \ldots N_j!\, \sigma_1^{N_1} \sigma_2^{N_2} \ldots \sigma_j^{N_j}} \quad . \quad . \quad . \quad . \quad (61)$$

If instead of a *gas-mixture*, as in our case, a *single gas* of monatomic [4]) molecules is considered, this factor $\mathfrak{P}$ reduces to

$$\mathfrak{P} = \frac{X!}{X!} = 1 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (62)$$

---

[1]) O. STERN, quite recently remarks: "The difficulty in this deduction lies in the introduction of the quantity N, which is done in a very arbitrary manner". (Z. f. Elektroch. **25** (1919), p. 79 at the top on the right).

[2]) Comp. our remarks in notes (1) and (2) § 5 with regard to the quantities Ω and I, which in our theory occur in the entropy and in $log\{\gamma\}$.

[3]) As regards the theories of LENZ (Vorträge der Wolfskehl-Stiftung 1913 in Göttingen, Teubner 1914, p. 125) and KEESOM (Phys. Ztschr. 14 (1913), p. 212), who apply DEBIJE's method for solids to gases, we may refer to papers by H. A. LORENTZ (Versl. Kon. Ak. v. Wet. Amst. 23 (1) (1914) p. 515, § 6 — Proceedings Amsterdam **19**, (1917) p. 737) and O. STERN (Ztschr. für Elektrochemie, **25** (1919), 79 section C towards the end), where these theories are discussed.

[4]) The same holds for a gas with more atóms in the molecule, if $\sigma = 1$.

The question, therefore, is how those authors, who confined themselves to the consideration of a single gas, were able to obtain a "thermodynamic probability", the logarithm of which yields an admissible entropy-equation, in other words, how do they manage, that the entropy does not contain a term of the form

$$R \log V \quad \text{but} \quad R \log \frac{V}{n_i}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (63)$$

1. O. SACKUR[1]) reaches the desired result by a special method of "quanticising" the motion of the gas-molecules: we may express it by saying, that he quanticises, as if each molecule were separately contained in a cell of volume $\frac{V}{N_i}$.

2. M. PLANCK[2]) similarly only obtains the term (63) in the correct form by dividing the phase-space of the molecules (μ-space) into an increasing number of "elementary" portions, as the number of molecules is larger ($G = Ng$). The justification of this procedure and the fixing of g he considers to be open problems[3]).

3. H. TETRODE [1st Paper][4]) attaches a factor $\frac{1}{N_i!}$ to the expression for the "thermodynamic probability", *in order that* its logarithm may show the law of dependence on N which is needed in the entropy. But he does not justify this procedure on combinatory grounds[5]).

---

[1]) O. SACKUR, Annalen d. Physik, **40**, p. 76 (1913).

[2]) M. PLANCK, Wärmestrahlung, 2 Aufl. § 126, § 133.

[3]) M. PLANCK, Theorie der Wärmestrahlung, 2 Aufl. p, 131; also M. PLANCK Vorträge der Wolfskehl-Stiftung 1913 in Göttingen (Teubner 1914) p. 7; Phys. Zeitschr. **14** (1913), p. 258. In a later paper (Sitzber. d. Preuss. Akad., Berlin, 1916, p. 653—667) PLANCK once more returns to the problem; here he takes into account the permutability of the molecules, but he does not himself look upon this discussion as giving a combinatory justification of his assumption as to the "elementary regions".

[4]) H. TETRODE, Ann- d. Phys. **38**, p. 434 (1912).

[5]) H. A. LORENTZ, (Versl. Kon. Ak. v. Wetensch. Amsterdam **23** (1) (1914, p. 515, — Proceedings Amsterdam **19**. (1917), p. 737), at the end of section 5 draws attention to this. H. TETRODE in his 2nd paper, where he gives the new deduction by means of the process of evaporation, à propos of LORENTZ's remark in an appendix once more returns to his previous deduction. But again he explains — only more fully — that the division by the factor N_i ! is required, *in order that* the entropy may show the desired law of dependence on N_i. P. SCHERRER, Gött. Nachr. 1916, p. 154 in following the same procedure simply refers to J. W. GIBBS, Statistical Mechanics without any further comment.

ADDITIONAL NOTES.

I. *Elucidation of the choice of the μ- and γ-weight*: $\{\mu\}$ *and* $\{\gamma\}$. (*Note to sections* 2, 4).

The definitions of $\{\mu\}$ and $\{\gamma\}$ may be elucidated by a simple example. Consider first a PLANCK-resonator. According to the theory of quanta its phase q,p must lie either at $q = p = 0$ or on one of PLANCK's ellipses $\varepsilon = h\nu$, $2h\nu, \ldots$ Now two consecutive ellipses are known to enclose a ring whose area is

$$\iint dq\, dp = h \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (64)$$

The classical theory would admit all the points of the plane and ascribe to any portion of it a "weight" equal to its area $\iint dq\, dp$. It therefore seems natural in the statistical calculations of the quantum-theory to ascribe a weight h to each of the ellipses, *in particular also to the point* $q = p = 0$. Since in all statistical calculations it is ultimalely only the relative weight that matters, the essential thing about this assumption is, that the same weight is ascribed to all the ellipses, which moreover is independent of the nature of the resonator (say its ν). [1])

The choice of h itself as the weight in question has the following advantage in connection with (64): if in the q, p plane any portion is considered which contains a large number of ellipses, the total weight of all the ellipses inside this region coincides with its area owing to (64). [2])

Let us next consider a material point elastically connected to a given position of equilibrium, say anisotropically. Its principal vibrations may be parallel to the co-ordinates q_1, q_2, q_3, its frequencies being supposed very different

$$\nu_1 \ll \nu_2 \ll \nu_3 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (65)$$

---

[1]) The choice of the weight must be subjected to certain limitations, in order that the statistical theory may not get into contradiction with the IInd law of thermodynamics. Comp. P. EHRENFEST, Phys. Zeitschr. **15** (1914), p. 657; Ann. de Phys. **51** (1916), p. 340, § 8 — Versl. Kon. Ak. v. Wetensch. Amsterdam **25** (1) (1916), p. 423, § 8 — Proceedings Amsterdam **19** (2 part.) (1917), p. 576, § 8. — The above choice is in accordance with the limiting conditions in question.

[2]) Hence for sufficiently high temperatures we shall have approximately

$$\sum_0^\infty h e^{-\frac{\varepsilon_n}{rT}} = \int_{-\infty}^{+\infty}\int dp\, dq\, e^{-\frac{\varepsilon}{rT}}.$$

The μ-point of the system in the six-dimensional μ-space $(q_1, \ldots p_3)$ is then limited by the quantum-hypothesis in the following manner: its projection on the plane q_1, p_1 must fall on one of the PLANCK-ellipses; similarly the projections on the planes q_2, p_2 and q_3, p_3. If the total energy E is contained between 0 and a moderate value, we see by (65) that q_1, p_1 may still fall on a large number of different ellipses; (since for this degree of freedom the energy-stages $\varepsilon_1 = 0, h\nu_1, 2h\nu_1, \ldots$ follow each other closely), q_2, p_2 on the other hand only on a few ellipses, whereas q_3, p_3 is possibly completely confined to the position $q_3 = p_3 = 0$.

If the limitation which is due to the quantum-hypothesis did not exist, the "weight" to be given to a given region in the μ-space would according to BOLTZMANN simply be its volume

$$\int \ldots \int dq_2 \ldots dp_3 \quad . \quad . \quad . \quad . \quad . \quad . \quad (66)$$

To each region, whose three projections are three PLANCK-ellipses, we assign the weight

$$h^3 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (67)$$

The joint weight of all phases which the μ-point can assume, when the energy is subjected to an upper limit, will then be

$$\{\gamma\} = \sum_{\tau_1} \sum_{\tau_2} \sum_{\tau_3} h^3, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (68)$$

where the summations are to be extended over all the quantum-numbers which the first, second and third degree of freedom can assume. With a moderate upper limit for the energy τ_1 as we saw would be able to rise to high values, and the corresponding sum may accordingly be replaced by $\iint dq_1\, dp_1$; τ_3 on the other hand would be confined to zero and the corresponding sum reduce to the first member h. Hence

$$\{\gamma\} = \iint dq_1\, dp_1 \,.\, (\sum_{\tau_2} h) \,.\, h; \quad . \quad . \quad . \quad . \quad . \quad . \quad (69)$$

According as the upper limit for the energy is made to rise or fall (i.e. the second degree of freedom is made to pass from the state of being half-excited to that of full excitation or non-excitation) (69) changes into

$$\{\gamma\} = \int \ldots \int dq_1\, dp_1\, dq_2\, dp_2 \,.\, h = h^{3-2} \int \ldots \int dq_1 \ldots dp_2 \quad . \quad (70)$$

or

$$\{\gamma\} = \iint dq_1\, dp_1 \,.\, h \,.\, h = h^{3-1} \iint dq_1\, dp_1 \quad . \quad . \quad . \quad . \quad . \quad . \quad (71)$$

Evidently of all the original degrees of freedom only those remain in the power of h, which are not excited. The other factors h are as it were absorbed by the intregrals.

II. *Calculation relating to* § 6.

We found [eq. (27) § 5].

$$\left.\begin{aligned} log\{\gamma\} = I + \Sigma N_i\left[log\, V + \frac{f_i}{2} log\, K + log\, \alpha_i'\right] \\ - \Sigma N_i (log\, N_i - 1) - \frac{F}{2}\left[log\frac{F}{2} - 1\right] \end{aligned}\right\} . \quad (72)$$

If this expression is varied, having regard to

$$\delta V = 0, \qquad \delta N_i = \nu_i\, \delta Q, \qquad \delta E = \delta K + \Sigma \chi_i\, \delta N_i = 0, \quad . \quad (73)$$

the last equation provided with a multiplier $(-\theta)$ being added to the variation of $log\{\gamma\}$, we obtain:

$$\left.\begin{aligned} 0 = \delta log\{\gamma\} - \theta\, \delta E = \frac{\delta K}{K}\Sigma N_i \frac{f_i}{2} + \Sigma \delta N_i\left[log V + \frac{f_i}{2} log\, K + log\, \alpha_i'\right] \\ - \delta Q \Sigma \nu_i log\, N_i - \left(log\frac{F}{2}\right)\delta Q . \Sigma \nu_i . \frac{f_i}{2} - \delta K - \delta Q . \Sigma \nu_i \chi_i - \end{aligned}\right\} \quad (74)$$

The condition that the co-efficient of δK disappears, gives:

$$\theta = \frac{F}{2K}; \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (75)$$

that for δQ

$$\Sigma \nu_i log\, N_i = \Sigma \nu_i\left[log V + \frac{f_i}{2} log\, K + log\, \alpha_i' - \frac{f_i}{2} log\frac{F}{2} - \theta\, \chi_i\right], \quad (76)$$

or by (75) after a small reduction

$$\Sigma \nu_i log\, N_i = \Sigma \nu_i\left[log\, V + \frac{f_i}{2} log\frac{2K}{F} + log\, \alpha_i' - \frac{F}{2K}\chi_i\right], \quad . \quad (77)$$

q. e. d.

The thermodynamical calculation is entirely similar.

III. *Deduction of the vapour-pressure formula for very low temperatures.*

The equilibrium of evaporation at very low temperatures may be deduced by the same means as that of dissociation. If again there are X, Y, Z atoms in a volume V, which, however, may now be associated in N poly-atomic molecules of one kind, of composition ξ, η, ζ, mass and moment of inertia M, P, Q, R and symmetry-number σ, N of these may be present in the form of vapour

(potential energy $= N\chi$) and N' condensed to a crystal (potential energy $= N'\chi'$).

For the vapour molecules we make again the assumptions I and II of section I. As regards the atoms in the crystal our assumption will be, that

III. In the calculations the motions of the atoms in the crystal are to be ignored [1]).

The $\{\gamma\}$ weight of the condition (N, N') is then found to be

$$\{\gamma\}=\frac{X!\,Y!\,Z!}{N!\,\sigma}h^{3(X+Y+Z)-6N}V^N.\frac{1}{\Gamma(3N)}.(\sqrt{2K\pi})^{6N}.(4\pi.2\pi\sqrt{M^3PQR}), \quad (78)$$

where

$$K=E-\Sigma(N\chi+N'\chi') \quad . \quad . \quad . \quad . \quad . \quad . \quad (79)$$

On the other hand the entropy and energy of the system are given by the equations

$$S=\overline{\Omega}+n\left\{C\log T+R\log\frac{V}{n}+\varkappa\right\}+n's_0' \quad . \quad . \quad (80)\text{ [2])}$$

$$E=n\{CT+b\}+n'b'. \quad . \quad . \quad . \quad . \quad . \quad . \quad (81)$$

The condition of equilibrium is given by

$$\delta\log\{\gamma\}=0. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (82)$$

with the conditions

$$\delta V=0, \qquad \delta E=0, \qquad \delta N+\delta N'=0, \quad . \quad . \quad . \quad (83)$$

This yields an equation for N' as a function of V and K; substituting

$$K=3N.rT \qquad V=N.\frac{rT}{p} \quad . \quad . \quad . \quad . \quad . \quad (84)$$

we find

$$\log p=-\frac{\chi-\chi'}{rT}+4\log T+\alpha, \quad . \quad . \quad . \quad . \quad . \quad (85)$$

where α has the same meaning as α, in (46). The corresponding thermodynamic calculation gives

---

[1]) This assumption is again meant not as a physical hypothesis, but as an approximation in the calculations. (Comp. note 5, § 1). It comes to neglecting $\int_0^T \frac{C'}{T}\,dT$ for the solid (comp. M. PLANCK, Thermodynamik, 4 Aufl., § 288, comp. (270) in the thermodynamic deduction of the vapour-pressure formula for low temperatures.

[2]) Properly speaking the last term should be $n's'$; but with PLANCK we neglect $\int_0^T \frac{C'}{T}\,dT$.

$$\log p = -\frac{b-b'}{RT} + \frac{C_p}{R}\log T + \frac{a-s_0'}{R}, \quad . \quad . \quad . \quad . \quad (86)$$

where for shortness we have put

$$\varkappa - C_p + R\log R = a \quad . \quad . \quad . \quad . \quad . \quad . \quad (87)$$

The comparison of (85) and (86) produces the equation

$$\frac{a}{R} = \alpha + \frac{s_0'}{R} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (88)$$

or for molecules of different kinds

$$\frac{a_i}{R} = \alpha_i + \frac{s_{01}'}{R} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (89)$$

Nernst's theorem requires for every chemical reaction $\nu_1, \nu_2 \ldots \nu_j$, which is possible the relation

$$\Sigma\, \nu_i s_{0i}' = 0, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (90)$$

which is satisfied by

$$s_{0i}' = \xi_i u' + \eta_i v' + \zeta_i w' \quad . \quad . \quad . \quad . \quad . \quad . \quad (91)$$

where $u'v'w'$ remain perfectly arbitrary.

Evidently the chemical constant as calculated by means of the vapour-pressure formula and Nernst's theorem contains similar indeterminate contributions by the atoms as in our deduction from the dissociation-equilibrium.

Physics. — "*The osmotic pressure, regarded as a capillary phenomenon*". By H. HULSHOF. (Communicated by Prof. H. A. LORENTZ).

(Communicated at the meeting of March 27, 1920).

In this paper an attempt will be made to give an explanation of the osmotic pressure by regarding this pressure as the consequence of capillary actions. Though some difficulties remain, in my opinion a trial in this direction might be made. In a former communication (these Proceedings January 1900) the surface tension has been defined. To that end we supposed at a point of the passage layer fluid-vapour the influence of the attraction in different directions to have different values. Now we shall base our considerations on the same suppositions. For a plane in the direction of the passage layer p_1 is the whole force per unit of surface (pressure) exerted by the matter on one side of the plane on that on the other side. It consists of the attraction q_1 and what may be called the thermic pressure ϑ, so that

$$p_1 = -q_1 + \vartheta.$$

For a surface element perpendicular to the passage layer we can also speak of the total force exerted by the part of the system on one side on the part on the other side. Let us call this p_2 and let us write q_2 for the attraction between the two parts and ϑ for the thermic pressure. Then we have:

$$p_2 = -q_2 + \vartheta.$$

Instead of the attraction q_1 and q_2 we may also consider the molecular pressure M_1' and M_2'; $q_1 = M_1'$ and $q_2 = M_2'$; in homogeneous phases $q = M' = a\varrho^2 = \frac{a}{v^2}$. The thermic pressure $\vartheta = \frac{MRT}{v-b}$ will be supposed to have in all directions a value equal to that in a homogeneous phase of the density at the point in question.

$$p_1 + M_1' = p_2 + M_2' = p + M' = \vartheta.$$

The index 1 refers to the direction perpendicular to the passage layer, the index 2 to a direction in this layer; as to gravity we assume that it only causes the layers to be horizontal; the height h is measured upward perpendicular to the passage layer. Differen-

tiating the different quantities with respect to h and taking into consideration that p_1 has a constant value, we obtain:

$$dM_1' = dp_2 + dM_2' = dp + dM'.$$

Omitting the constant we can write for the energy at the height h

$$\varepsilon = -a\varrho - \frac{c_2}{2}\frac{d^2\varrho}{dh^2} - \frac{c_4}{4!}\frac{d^4\varrho}{dh^4} \cdots,$$

where $\varrho = \frac{1}{v}$. Splitting this energy into a part ε', corresponding to the homogeneous phase and a part ε'', we may write

$$\varepsilon = \varepsilon' + \varepsilon''$$

Now the stationary equilibrium demands that both in the homogeneous phase and in the passage layers fluid-vapour and fluid-solid wall

$$\varepsilon - \tau\eta + p_2 v = \mu M$$

has a constant value. Here p_2 represents therefore the pressure in the direction of the passage layer; in the homogeneous phase it has the same value as the constant pressure in the vessel. The equation expresses that layers lying in each other's neighbourhood will exchange the same number of particles in the same time.

The change of the attraction (molecular pressure) in the direction of h from point to point is:

$$dM_1' = -2\varrho\, d\varepsilon = -2\varrho\,(d\varepsilon' + d\varepsilon'') = 2a\varrho\, d\varrho - 2\varrho\, d\varepsilon''.$$

This follows from the value of

$$M_1' = a\varrho^2 + c_2\varrho\frac{d^2\varrho}{dh^2} - \frac{c_2}{2}\left(\frac{d\varrho}{dh}\right)^2$$

in connection with

$$\varepsilon = \varepsilon_0 - a\varrho - \frac{c_2}{2}\frac{d^2\varrho}{dh^2}.$$

$$dp + dM' = dp + 2a\varrho\, d\varrho$$

and so $-2\varrho d\varepsilon'' = dp$ or $-2d\varepsilon'' = v dp$, whence $p - p_1 = -\int 2\varrho d\varepsilon''$.

For $\varepsilon - \tau\eta + p_2 v = \mu M$ we may write $\varepsilon' + \varepsilon'' - \tau\eta + pv + (p_2 - p)v = \mu M$. By differentiation we find $vdp + d\varepsilon'' + d(p_2 - p)v = 0$, as $d\varepsilon' - \tau d\eta + pdv = 0$; this is evident when we regard the unit of mass (as homogeneous phase) as having first had the volume v at the height h and afterwards the volume $v + dv$ at the height $h + dh$. For the passage from one state into the other we have:

$$\tau d\eta = d\varepsilon' + pdv.$$

As further $vdp = -2d\varepsilon''$, we have $-d\varepsilon'' + d(p_2 - p)v = 0$ and so

$$\varepsilon'' = (p_2 - p)\, v \quad \text{of} \quad \varrho\varepsilon'' = p_2 - p.$$

Now we find:

$$p_1 - p_2 = -\varrho\varepsilon'' + \int 2\varrho\, d\varepsilon'' = \varrho\varepsilon'' - \int 2\varepsilon''\, d\varrho.$$

Therefore

$$dp_2 = \varepsilon'' d\varrho - \varrho d\varepsilon'',$$

for which we may always write:

$$dp_2 = \varepsilon d\varrho - \varrho d\varepsilon.$$

Still it may be remarked, that when the condition of the thermodynamic theory that $\int \frac{\psi - \mu M}{v}\, dh$ shall be a minimum, is satisfied (the integration has here to be extended over the whole depth of the passage layer), one element of this integral is just equal to $-p_2, p_2 - p = \varrho\varepsilon''$ and $M_2' = -\varrho\varepsilon$.

Suppose, we had started from the definition of the molecular pressure in the direction of the bounding layer that it was equal to $-\varrho\varepsilon$ (with omission of the constant). Then this would evidently have led us to a value of the surface tension in agreement with the thermodynamic theory, which is a proof of the validity of the definition. But then we can at once write down the differential equation for the surface tension. For from

$$p_1 - p_2 = M_2' - M_1'$$

it follows directly that

$$-dp_2 = -d\varrho\varepsilon + 2\varrho d\varepsilon = -\varepsilon d\varrho + \varrho d\varepsilon.$$

When a fluid is in contact with a solid wall, the molecular pressure and therefore also the external pressure in the perpendicular to the passage layer will generally be different from the pressure in the direction of this layer. The action of the solid wall on the fluid at the wall influences the molecular pressure of the fluid at the wall. External forces like gravity, a magnetic or electric force will directly influence the external pressure. As also in this case the molecular pressure in the direction of the passage layer M_2' may be represented by $-\varrho\varepsilon$ and as $dM_1 = -2\varrho d\varepsilon$, we have here likewise:

$$d(p_1 - p_2) = -dp_2 = -d\varrho\varepsilon + 2\varrho d\varepsilon = \varrho d\varepsilon - \varepsilon d\varrho.$$

The calculation of the value of the molecular pressure of the fluid at the wall presents great difficulties, because the calculation is based upon the continuous division of the matter. In the immediate neighbourhood of the wall e. g. the value of the molecular pressure in the direction of the wall will be caused by the attraction of the wall and of the fluid, but in the case of equal spheres of action the contribution of the two will be due to unequal volumes. The

difference of these volumes will be intimately connected with the dimensions of the molecule. Moreover, except with regard to the attraction, a solid wall impenetrable for the particles is quite different from a fluid wall formed by the particles themselves.

Let us consider a very much diluted solution e. g. a solution of sugar in water, the vapour phase of which does therefore not contain the solved substance. The concentration x will then decrease in the passage layer from x_1 in the homogeneous solution to zero at the vapour side. In the passage layer near the solid wall too the concentration will change and in very different cases a similar change of the concentration must occur as in the passage of fluid to vapour, viz. from x_1 to zero in the layer next to the solid body. Now it is important to consider what will happen to the pressure p_2 (in the direction of the surface layer) *especially in the layer next to the solid wall* in which the concentration will be regarded as zero, when the concentration within the solution is increased from x_1 to $x_1 + dx_1$. Here therefore we have not to do with the change in *the total surface tension* of the solution when in contact with the solid wall $\int (p_1 - p_2)\, dh$, but only with the change of p_2 in the layer next to the wall. When the concentration is increased by dx_1, the potential of the solvent decreases. For when we have the solution under the pressure of the saturated vapour, the thermodynamic potential of the vapour decreases by $v_d\, dp$, when dp is written for the decrease of the vapour pressure and v_d for the specific vapour volume. In the uppermost layer of the passage layer next to the vapour the decrease of the thermodynamic potential is $v_d\, dp_2' = v_d\, dp$, as here too $dp_2' = dp$. Also in the layer next to the solid wall the thermodynamic potential will decrease by the same amount. This decrease may be due for the greater part to a decrease of p_2 in the immediate neighbourhood of this wall, where just as in the vapour no dissolved matter is present, so that a change of x can have no influence, as here x is zero. This is a tempting supposition, as in this case $v_d\, dp$ would be equal to $v dp_2$, when v represents the specific fluid volume of the pure solvent near the wall. However this may be, it is certain that p_2 will change at the wall when the concentration is altered.

Let us consider two glass vessels, both filled with the same diluted solution of sugar in water of exactly the same concentration. The vessels should be connected by a tube part of which is so narrow that no sugar molecules can pass through it, as their distance from the

wall cannot not be great enough. This part therefore contains only the outer layer of the passage layer. In this case the pressure p_2 close to the wall and in the direction of the wall will be the same everywhere both in the vessels and in the tube. Now when in the vessel on the left the concentration is increased by an amount Δx_1, then in every part of the left vessel as far as the narrowing of the tube, the pressure along the wall will have diminished by an amount Δp_2; the equilibrium is destroyed, in the narrow part we now have a fall of pressure, which will cause a current of pure water through the narrow part from right to left. By preventing the solution in the left vessel from occupying a greater volume, the equilibrium will be established again by the displacement of some water. Owing to this the pressure in the left vessel will increase everywhere *in all directions* by the constant amount Δp_2, so that the pressure along the wall in this vessel will again become p_2, and the equilibrium will be established again. This increase of pressure Δp_2 is what is usually called the osmotic pressure, the over-pressure in the left vessel. Now when in the right vessel no sugar is present, so that in the left vessel there is already an osmotic pressure corresponding to the small concentration x_1, we may say, that the *decrease* of the pressure p_2 along the wall caused by an increase dx_1 of the concentration is equal to the *increase* of the osmotic pressure due to the capillary action.

From the experiment we know that $\Delta p_2 = \frac{MRT}{v} \Delta x_1$, where Δp_2 has been written for the osmotic pressure. When Δp_2 represents the change of pressure along the wall, we may write $-\Delta p_2 = \frac{MRT}{v} \Delta x_1$. In this last relation v is the volume of M_1 grams of pure solvent under the pressure of the vessel. We may write for it: $v' - x_1 \left(\frac{dv'}{dx}\right)_p$, where v' is the volume occupied by $M_1 (1-x)$ grams of the first component and by $M_2 x$ grams of the second under the same pressure.

In the equation

$$v \Delta p_2 = - MRT \Delta x_1$$

the right hand side represents also the change of the thermodynamic potential, when the concentration increases by Δx_1, while the pressure remains constant. The theory of VAN DER WAALS namely gives for the value of this potential in the homogeneous solution

$$\mu M = MRT \log (1-x_1) + \mu_{x_1} - x_1 \left(\frac{d\mu_{x_1}}{dx_1}\right)_p.$$

Here is

$$\mu_{x_1} = pv' - \int p dv' = pv' - MRT \log (v' - b_{x_1}) - \frac{a_{x_1}}{v'}.$$

So

$$\left(\frac{d\mu M}{dx_1}\right)_p = -\frac{MRT}{1-x_1} - x_1 \left(\frac{d^2\mu_{x_1}}{dx_1^2}\right)_p$$

and as we confine ourselves to very diluted solutions

$$\left(\frac{d\mu M}{dx_1}\right)_p = -MRT$$

We find therefore the relation

$$v \Delta p_2 = \Delta \mu M.$$

The value of the thermodynamic potential of the solvent at the wall, where we take $x =$ zero, may be represented by

$$\varepsilon - \tau\eta + p_2 v = \mu M.$$

For a change of the value of μM therefore we have the relation

$$d\varepsilon - \tau d\eta + p_2 dv + v dp_2 = d\mu M.$$

When this explanation of the origin of the osmotic pressure is right then $v dp_2 = d\mu M$. And as the only change the state of the bounding layer in the immediate neighbourhood of the wall can undergo by an increase of the concentration of the homogeneous solution by dx_1 is a change in density, we must have for any such change

$$d\varepsilon - \tau d\eta + p_2 dv = 0.$$

But this consequence is in perfect correspondence with the thermodynamic theory of capillarity.

Let us consider an element of the outer layer and let us expand it, without changing its thickness, in the direction of the wall, so that v becomes $v + dv$. The external work done at the expense of the supplied heat is $p_2 dv$ and not $p_1 dv$. The supplied heat is $\tau d\eta$, so that we have:

$$\tau d\eta = p_2 dv + d\varepsilon.$$

In fact this equation is nothing but the well-known equation from the theory of capillarity:

$$d\varepsilon = \tau d\eta - p_1 dv + \sigma ds,$$

when we do not apply it to the layers as a whole, but to only one of the layers.

As our conclusion is right, we may evidently also treat the problem in another way viz. by assuming that we have

$$d\mu M = v dp_2$$

for an isothermic change in the outer bounding layers where we may suppose no sugar to be present.

Let us further assume that in the homogeneous diluted solution the quantity μM for the water has another form but always the same value as for the outer layer that consists of pure water (or in the vapour phase without sugar, that is in coexistence with the solution). This μM in the homogeneous solution is a function of x_1 and p_1;

$$\left(\frac{d\mu M}{dx_1}\right)_{p_1} = -\frac{MRT}{1-x_1} - x_1\left(\frac{d^2\mu_{x_1}}{dx_1^2}\right)_{v'T} \text{ and } \left(\frac{d\mu M}{dp_1}\right)_{x_1} = v' - x_1\left(\frac{dv'}{dx'}\right)_{p_1}.$$ [1])

when we increase the concentration of the sugar solution by dx_1 while the pressure p_1 remains constant, μM in the solution changes by $-MRTdx_1$, and in the outmost sugarless layer near the wall by vdp_2. From this it follows $vdp_2 = -MRTdx_1$. When we admit that osmotic pressure appears this will have the value

$$dp_2 = \frac{MRT\,dx_1}{v}.$$

Here it may be remarked, that by admitting the osmotic pressure, the pressure will in all directions increase by the amount dp_2. In the outer bounding layer the pressure p_2 thus gets its original value again. The total change of p_2 because of the two changes of state is therefore zero.

The same is therefore the case with μM in the outer bounding layer as $d\mu M = vdp_2$. Also for the total change of μM in the homogeneous solution, so that

$$\left(\frac{d\mu M}{dx_1}\right)_{p_1}\Delta x_1 + \left(\frac{d\mu M}{dp_1}\right)_{x_1}\Delta p_1 = 0,$$

where $\Delta p_1 = \Delta p_2$. By means of this relation HONDIUS BOLDINGH derived the formula of the osmotic pressure from thermodynamic considerations.

The decrease of pressure in the layer at the solid wall may be compared with the decrease of vapour pressure. When the solved substance occurs neither in the vapour phase nor in the outmost layer at the solid wall, there will always be a decrease of vapour pressure and of the pressure at the wall in the direction of this wall according to the simple laws for very diluted solutions. To a definite solved substance in a definite solvent a wall will be semipermeable, when the pores in this wall are so narrow that only the solvent substance can enter into them and not the solved substance. It is evident that changes of temperature and pressure can also have influence on the semipermeabi-

[1]) See Dr. G. HONDIUS BOLDINGH. Thesis. Amsterdam 1893.

lity. The layer of ferrocyancopper in the porous pot will generally stop the wide pores. The pores through which neither coppersulfate nor potassium ferrocyanide can pass, remain open, but we may expect that between the ferrocyancopper formed and the wall of the porous pot holes narrow enough will remain and moreover that in the layer of ferrocyancopper there will remain narrow holes fit for the semipermeability. Where this layer is formed, the concentration of the two solutions locally decreases considerably, so that probably the layer will not be continuous, leaving holes narrow enough for semipermeability.

Also when the concentration of the solution near the wall is not zero, or when the pores are somewhat too wide osmotic phenomena may occur. Then, however, the simple law will no longer be valid; the semipermeability will not be perfect and by pressing the solution we shall not obtain the pure solvent through the pores, but a solution, though perhaps of lower concentration than the one under the pressure.

The decrease of the melting point may illustrate the above considerations, also because we have indications here, that at a solid wall the concentration of a solution can be zero. Let us consider the solution at such a temperature that there is also ice present in the sugar solution. The ice is separated from the solution by a layer of pure water, in which the pressure close to the wall is p_2. When the solution is frozen, generally pure water on the surface of the ice is frozen. This indicates that *probably in the layer surrounding the ice the solved substance does not occur*. Now when under constant pressure the concentration x_1 is increased by dx_1, the pressure p_2 changes by such an amount that $vdp_2 = -MRTdx_1$, where v is therefore the specific volume of the water next to the ice. Now the solid wall is a wall of ice, which must be in thermodynamic equilibrium with the water. When however the equilibrium is destroyed not directly between the ice and the solution, but between the ice and the layer of pure water surrounding the ice, in which layer the pressure p_2 along the ice surface and therefore also the difference in pressure $p_1 - p_2$ is changed, only a change of temperature can restore the equilibrium, can cause that the two phases in contact regain their coexisting equilibrium. A change of the temperature dt, will change the potentials of the water and of the ice by $-\eta_w\, dt$ and $-\eta_{ij} dt$. As $-\eta_{ij}\, dt$ is at the same time the total change of the thermodynamic potential of the ice, we shall have

$$-\eta_{ij}\, dt = -\eta_w\, dt + v\, dp_2.$$

As further $\eta_\omega - \eta_y = \frac{\lambda}{t}$, where λ represents the melting heat, this relation becomes

$$\frac{dp_2}{dt} = \frac{\lambda}{vt}.$$

dp_2 is negative. We have thus a sinking of the melting point and there is no osmotic pressure. The osmotic action appears only when after having prevented the volume from increasing we bring, the whole system into semipermeable connexion with a solution of the original concentration x_1 and under the pressure of the system. The pressure in this whole system increases everywhere and in all directions by an amount just equal to $-dp_2$ (a positive amount). Except for the sign the formula for the sinking of the melting point therefore becomes the same, or, when dp is written for the increase of the osmotic pressure,

$$\frac{dp}{dt} = -\frac{\lambda}{vt}.$$

Zoology. — *"Technical experiences in the breeding of Tenebrio molitor"*. By S. A. ARENDSEN HEIN. (Communicated by Prof. J. W. MOLL).

(Communicated at the meeting of April 23, 1920).

Studies on variation in Tenebrio molitor, of which the results are published in the Journal of Genetics, gave occasion to make some observations with respect to the practice of the breeding of this insect. Though these facts are not very suitable for being treated in a genetical periodical, as they deal especially with technical particulars, I thought their publication to be of some value for those who wish to experiment with this beetle.

CONTENTS.

1. Choice of the culture vessels.
2. The food.
3. The number of moults of the larva.
4. The infection with Tyroglyphus farinae
5. The gathering of Pupae and beetles.
6. The gathering of the Eggs.
7. The mortality. *a.* amongst the Eggs.
b. ,, ,, Larvae.
c. ,, ,, Pupae,

1. *Choice of the culture vessels.*

Larvae. For the culture of larvae, glass crystallizing jars are preferable to any other kind. From these jars with their perpendicular slippery wall the larvae cannot escape.

Porcelain pots with perpendicular smooth walls also give satisfaction. Tin boxes with lids not fitting too close (for the air circulation) are serviceable only when the inner wall is perfectly smooth (not varnished or painted), without any rust-stains, solder or rough connecting seam, so that the larvae lack any support in crawling up the wall.

The fulfilment of these conditions is of great importance when the perfect purity of the cultures is aimed at. Close attention should

be paid to these conditions in order to preclude unpleasant surprises. Glass jars guarantee against any disappointment.

As the larvae thrive better when the layer of food is not too thick, the quantity of larvae that can be accommodated in a vessel depends on the size of the bottom rather than on the capacity. As a minimum about 20 sq. centimetres (3 or 4 sq. inches) should be available for every 100 larvae.

For a quick growth and early pupation the food is to be renewed at set times. The need of a renewal becomes clear from the crumbly powdery state into which the scaly structure of the bran has passed.

The renewal is brought about most effectively by sieving.

A suitable form of sieve is found among the common kitchen utensils (cf. sketch). The material is usually tin, the inner side and bottom smooth, the latter (no wire-sieve) perforated with round holes of 2 or 3 millimetres diameter according to the size of the larvae.

By shaking the sieve horizontally and quickly, the larvae remain in a horizontal position, have no opportunity of erecting themselves and are left behind on the bottom, even when their thickness is smaller than the diameter of the holes.

In less than no time a large culture of some thousands of larvae can be separated from the bran and provided with fresh food.

For cultures of which the larvae are very small yet, very fine wire-sieves should be used. This practice should, however, be stopped as soon as possible as the food, defiled by faeces, is not sufficiently cleared by these fine sieves.

The larvae jars were covered with a glass plate. By glueing two strips of thick cardboard firmly on this plate, an interstice is left between the rim of the jar and the glass plate through which opening an adequate air-circulation can take place. If these cardboard strips are laid loose, and if by shoving away or removing the jar, such a strip falls with one end into it, the larvae immediately utilise it as a bridge to escape, and before one thinks of it, the jar is empty.

2. *The Food.*

Relying on the statement occurring here and there in the literature (Frenzel p. 298) on this subject to the effect that bran should be a sufficient food for larvae, bran was given at the outset. Their growth, however, was not satisfactory. Then a substance containing

more fat, in the form of rusk, was added by way of trial. According to the number of larvae one or more whole rusks were put in the larvae jars. The creatures took them with eagerness. For comparison some other jars were provided with some slices of peat. Also under these, the larvae gather up and they make large passages in the peat. It is not probable that the peat should serve them for food. After this experience the following comparative experiments were made.

Six jars were provided with:

N°. 1 only bran . . . . . (B.)
N°. 2 bran on a layer of peat . . . . . (B.P.).
N°. 3 only meal (flour) . . . . . (M.).
N°. 4 meal (flour) on a layer of peat . . . . . (M.P.).
N°. 5 bran with rusk . . . . . (B.R.).
N°. 6 meal (flour) with rusk . . . . . (M.R.).

In each jar 300 eggs were placed in the same period (May 27—June 21 1915). Down to February 10, 1916 included, the following numbers of pupae were collected:

TABLE I.

Number of jar.	Food.	Number of Larvae obtained from 300 eggs	Pupae collected till Febr. 10. 1916 incl.	Number of Pupae in Per-cent. of the larvae.
1	B.	250	0	—
2	B. P.	172	0	—
3	M.	247	3	1.2 %
4	M. P.	192	13	6.7 „
5	B. R.	206	43	20.8 „
6	M. R.	225	36	16 „

From the foregoing figures, though provisional, the following conclusions may be drawn.

1. An exclusive nutrition of bran is inadequate to a normal growth of the larvae.

2. An exclusive nutrition of meal is better than bran alone.

3. An addition of rusk to meal or bran promotes the development of the larvae considerably.

4. An addition of rusk gives a better result to bran than to meal; the pupation is 4 per cent higher.

This provisional result was again tested in the following manner.

TABLE II.

Number of jar	Number of Larvae on Febr. 10 1916	Food	Pupae gathered in: Total on April 20 1916	Pupae gathered in: Total on July 8 1916	% of the Larvae on April 20 1916	% of the Larvae on July 8 1916	Remaining Larvae on April 20 1916 Living	Remaining Larvae on April 20 1916 Dead	Remaining Larvae on July 8 1916 Living	Remaining Larvae on July 8 1916 Dead	Weight of Larvae in milligrams Total	Weight of Larvae in milligrams per Larva	Mortality of Larvae on 100 Larvae
	1	2	3	4	5	6	7	8	9	10	11	12	13
1*a*	125	B	0	—	0	—	118	7	—	—	—	—	5.6 %
1*b*	125	B + R	53	—	42.4 %	—	—	—	—	—	5803	170	—
3*a*	98	M	—	35	—	35.7 %	—	—	41	22	2911	63	22.4 %
3*b*	98	M + R	—	64	—	65.3 %	—	—	31	3	3609	116	3 %
	on April 20 1916												
2*a*	52	B + P	0	0	—	—	—	—	31	21	1850	59	40 %
2*b*	52	B + P + R					—	—	51	1	5811	114	2 %

On the 10th of February 1916 the larvae of N°. 1 (B) and N°. 3 (M) were sieved, and each group was divided into two halves of an equal number of larvae. The same process was applied to N°. 2 (B.P.) on April 20, 1916.

The 6 groups of larvae were put in separate jars. To 3 of these (half of each group) rusk was added; the 3 other jars kept the old food without rusk.

On April 20, 1916, i.e. 69 days after the above-mentioned division, the pupae collected from the sub-groups of N°. 1 were counted, and on July 8, 1916, i.e. 48 days after the division, the pupae of the sub-groups of N°. 3. The group N°. 2 had not yet yielded any pupae. The remaining living larvae were weighed on a chemical balance. The result of this is shown in the following tabular statement.

Here too, the four conclusions drawn from the first experiment (Table I) may be maintained unabated. That the addition of rusk to meal is very effective is manifest, not only from the more numerous pupation (30 % more), but also from the absolute weight of the remaining larvae, which for M + R is nearly twice as great as for M alone. The enormous difference in the mortality of the larvae is also remarkable.

Until now the rusks had always been added unbroken.

A special reason gave occasion to putting the question whether rusk would operate as favourably if reduced to dust and mixed with the bran. Indeed, from former experiments (not undertaken for food purposes) the experience had been made that larvae fed exclusively on pulverised rusk (rusk meal), do not grow, and many die. The increase of the body weight of the larvae fed on rusk alone amounted to 48 % in 43 days with a mortality of the larvae of 38 %, whereas the figures for the larvae fed on bran appeared to be 117 % with a mortality of only 1.5 %.

The food experiments were therefore continued with the following modifications. The 118 larvae which remained on the 20th of April 1916 of experiment N°. 1*a*. (cf. Table II, column 7), i.e. larvae fed exclusively on bran, were again divided into two equal halves, each of 59 larvae. With one of these halves the old way of feeding (only bran) was kept up, the other half received bran + ruskmeal.

On the 8th of July 1916 the larvae of both groups were removed and weighed on a chemical balance. Pupae were not gathered from these groups between April 20 and Juli 8. (Table III).

The result obtained was as follows.

TABLE III.

		Numb. of Larvae on April 20	Food	Remaining Larvae on July 8		Mortality of Larvae on 100 Larvae	Weight of Larvae in milligrams	
				Living	Dead		Total	Per Larva
N°. 1*a*	N°. 1*a* 1	59	B	51	8	13 %	2565	50
	N°. 1*a* 2	59	B + Ruskm.	59	0	—	8114	137

It is obvious that the additional food administered in the form of pulverised (ground) rusk has operated very favourably, and in general no less than in the experiments with unbroken rusks. (Table II).

So far the experiments on the influence of rusk (fat) as additional food.

Now the question had to be settled whether bran, or bolted meal (flour) either with or without the addition of rusk, is of equal nutritive value to the larvae.

For this purpose it is necessary to revert to the jars N°. 4 (M.P.) N°. 5 (B.R.) and N°. 6 (M.R.) mentioned in Table I.

From these groups the following numbers of pupae had already been gathered on the Febr. 10, 1916 (as stated in Table I)

from N°. 4 (M.P.) 13 pupae.
N°. 5 (B.R.) 43 „
N°. 6 (M.R.) 36 „

The collecting of pupae was continued till July 8. Then the experiments were closed, the collected pupae counted, the mortality of the larvae figured out, and the remaining larvae weighed. This yielded the following results, also including those of experiment N°. 2*a* (of Table II), which may serve for comparison.

TABLE IV.

Number of experiment	Food	Nr. of Larvae at the beginning of the experiment	Pupae gathered		Remaining Larvae		Larval mortality to 100 Larvae.	Weight of the Larvae in m.gr.	
			Total.	in % of the Larvae	Living	Dead.		Total.	Per Larva.
5 (tab. I)	B. R.	206	149	72 %	4	53	25 %	619	155
6 (tab. I)	M. R.	225	118	52 „	50	57	25 „	5859	117
2*a* (tab. II)	B. P.	52	0	—	31	21	40 „	1850	59
4 (tab. I)	M. P.	192	39	20 „	11	142	74 „	835	76

From the above figures it is evident that bran with rusk a additional food had a much more favourable effect than meal + rusk;

the pupation is 20 % higher, the mortality of the larvae is equal, the weight of the remaining larvae is 38 milligrams per larva more.

This result could not be expected when at the outset it appeared (cf. Table I) that to meal and bran without any addition, meal was preferable; the addition of rusk shows the opposite, and this with rather strongly telling figures. It is probably only the fat and the albumin of the rusk that have operated so favourably.

Especially fat is only scantily found in bran and meal ($\pm$ 1.6 %), whereas the rusk used contained 8.9 %.

Summarizing the results of these nutrition experiments, they may be worded thus:

1. Exclusive meal food is preferable to exclusive bran food.

2. Rusk as additional food to meal as well as to bran always has a very favourable influence on the growth and the quicker development (pupation) of the larvae; this holds good for rusk in an unbroken or a ground state alike.

3. The most favourable results (more pupae, and low mortality and high weight of the larvae) were obtained by a mixed nutrition of bran + rusk.

4. Ground rusk as exclusive food for larvae is perfectly unsuitable. The mortality is considerable, the increase in weight small, the pupation is stopped.

5. The addition of slices of peat to meal or bran has no influence on the growth of the larvae, and is worthless as food. Peat seems to have a directly or indirectly noxious effect; the mortality is abnormally high.

3. *The number of moults.*

In the literature (Brehm p. 128; Frisch vol. III p. 1; Saling p. 2/8; Sturm p. 21/22) it is always stated, that the larva moults four times, and that after the fourth moult the pupa appears. Apparently this statement has never been controlled, for a simple experiment would immediately have shown, that it is false.

A larva was put in each one of a series of numbered small pots filled with fit food. The larvae were at most one or two days old, and still white in colour.

At fixed times these pots were searched for moults. The first moults are only to be found by carefully spreading out the food, and examining it with a lens. Notwithstanding a close inspection they sometimes escape notice, because they are often no longer intact, and broken up into smaller fragments, so that they are no longer to be recognized as moults.

Therefore the number of moults, given hereafter, is one or two moults more rather than less. When the larvae have grown larger and already show a distinct brown colour, these moults are easier to find; generally they lie on the surface of the food then.

The investigation gave the following result. During the first period of strong growth a moult may be expected every fortnight; afterwards this regularity ceases.

N°. 1 gave 11 moults; larval period 400 days; died without pupation.
N°. 2 gave 12 moults; larval period 194 days; normal pupation.
N°. 3 gave 10 moults; larval period 194 days; normal pupation.
N°. 4 gave 16 moults; larval period 405 days; normal pupation.
Larva N°. 5 gave 16 moults; larval period 376 days.

The investigation was repeated once more with 8 larvae, all of the same mother and of the same age.

Dates of the gathering.	Number of gathered moults from Larva							
	N°. 1	N°. 2	N°. 3	N°. 4	N°. 5	N°. 6	N°. 7	N°. 8
9th of November 1918 [1]								
28th " "	1	1	2	1	1	1	2	1
13th December "	1	1	1	1	1	1	1	1
29th " "	1	0	2	0	1	1	1	2
15th January 1919	1	2	1	1	2	2	2	1
31th " "	2	1	1	1	1	1	1	1
14th February "	1	1	1	1	1	1	1	1
28th " "	1	1	1	1	2	1	1	0
14th March "	1	1	2	1	1	2	1	1
30th " "	1	1	1	1	1	1	1	2
13th April "	1	1	0	1	1	0	1	1
30th " "	1	1	1	1	0	1	1	1
14th May "	1	1	1 [2]	1	1	1	1	1
Total of moults	13	12	14	11	13	13	14	13
Duration of larval period in days.	187	187	209	187	187	187	187	187

[1]) Date of the just emerging larva.
[2]) 26th May 1919.

The dates, on which the moults were gathered are also noted in the list before.

4. *Infection by Tyroglyphus farinae.*

Tyroglyphus farinae is a small mite strongly flattened dorsoventrally, about 0.4 millimetres long. The eggs of this mite seem always to be present in meal or bran, to develop only under definite circumstances, of which moisture seems to be the most important factor.

If the conditions of life are favourable to this mite, the multiplication may be so enormous that the whole layer of bran or meal seems to have changed into a homogeneous mass of Tyroglyphus.

It is true that this mite does not infest the larva, still the growth of the larvae is considerably injured by the withdrawal of food. The development of the pupae gathered from a jar infected with Tyroglyphus, also suffers great disturbances by this mite.

In close little heaps it nestles between and behind the legs, wings and antennae, and causes deformities of these organs in the later emerging beetles.

The researches with respect to Tenebrio were started in the spring of 1915 and continued without any incubators throughout the summer. The mite first made its appearance in 6 cultures at the same time, and that in jars which had been purposely placed in very damp surroundings; the development and multiplication of the mite in these jars was so intense that these cultures had to be done away with. Later on a similar experience was made with several other cultures standing free in the laboratory, when a spell of humid weather came. At first there seemed to be no better means than insulating these vessels from the rest. The necessity of this insulation to prevent all the cultures from being infected within a short time, is apparent from the fact that the infection passes from one jar to another in spite of their being covered with a glass plate, lying directly on the rim. The mite crawls up the wall of the glass, and tries to get out between the rim and the covering glass plate in which it generally succeeds, as there is always an interstice wide enough to allow its flat body to pass through.

Then an expedient was tried, which was efficacious so far as to prevent an infection from passing from vessel to vessel, even if they stand uncovered side by side.

At about 2 centimeters below the rim a ring of vaseline was applied inside.

Through this greasy substance the mite cannot get and the infection

remains limited to the jar in question, especially if the vaseline ring is thickened from time to time.

But restricting the extention of the infection is but an indirect measure against the evil, which may sometimes assume large dimensions, when its appearance must also be accounted for by the bad quality of the meal or the bran used. The experiences in this matter were at the outset so disappointing as to almost discourage any further investigations. So it stands to reason that with great satisfaction the experience was made that all at once everything changed for the better from the moment when the cultures were transferred into incubators with a temperature of ± 25° Celsius.

It sometimes occurred, it is true, that here and there the mite appeared (especially in humid weather), but by a general application of the vaseline ring, a sooner sieving and renewal of the food and an occasional raising of the temperature to 28°, the situation could be kept under control, so much so that Tyroglyphus farinae was no longer a formidable enemy.

5. *The Gathering of Pupae and Beetles.*

When the pupae make their appearance, they should be removed. Even if one does not wish to sort them into males and females, one has better not wait (for various reasons) until the beetles emerge.

When the layer of bran is not too thick the pupae work themselves up to the surface, either wholly, or partially, so that only the distal end of the abdomen sticks out above the bran layer. The sidelong broadened lateral edges of the segments 5 to 11 incl. (Fig. III) are provided with 3 or 4 sharp stings and wonderfully adapted to render this working up possible easily and quickly. That these broadened lateral edges with their stings are only serviceable in the pupae stage is apparent from the fact that this edge with the stings is cast off together with the pupal skin and does not return in the beetle. At a temperature in the incubator of 25° C, the larvae jars may, after the last gathering of pupae, stand 7 days, before they require to be inspected on pupae again. At the temperature mentioned the development from pupa to beetle takes about 9—12 days.

The pupae collected were put in deep saucers of a diameter of abt. 13 c.m., the bottom of which was covered with a patch of black sateen. As soon as the beetles emerge they crawl, shunning the light, under the patch or the curled-up borders of it. The number of cast moults that remain on the sateen, denotes the number of beetles that keep in the shade somewhere.

If the beetles need not be gathered daily, a piece of rusk should be laid under the patch. If no food is offered them in time, they eat the pupae.

The pupae dishes were covered with a glass plate reaching beyond the rim. In this way they may be piled up in the incubators, while any escape of the beetles is precluded.

6. *Gathering the Eggs.*

The collecting of the eggs was a matter of no small importance for the obtaining of a large posterity. The difficulties that were expected, did not occur; the problem was solved in quite a satisfactory manner. The beetles emerged in the pupae dishes are transferred to the beetleboxes in which the production of eggs is awaited.

The beetles were kept in tin boxes with smooth walls and provided with a cover closing not too hermetically. The bottom of the boxes is covered with a patch of black sateen, in which a few holes have been cut to let the beetles through, which hide by preference under the patch. On the top of the sateen small pieces of a woolly material are scattered. The choice of the quality of this material (egg patches) on which the eggs are deposited, is very important. On this point the beetles are very particular and will not at all, or only in a small number, deposit their eggs if the stuff is not woolly or thready enough, so that the ♀ cannot attach the eggs on it. If the stuff is too thready, the eggs are laid so deep in the tissue that they are difficult to discover. Also SALING records this peculiar habit of the beetles of depositing their eggs on a woolly material. The egg patches had a size of about 1 or $1^1/_2$ c.m^2. These small patches are preferable, for various practical reasons, to those of larger dimensions.

As food for the beetles, pieces of rusk were used, soaked with a few drops of milk, or fresh cut pieces of potato. Of the latter the beetles eat all but nothing; yet they greedily fall to them, probably attracted by the humidity of the food.

The food is put under the sateen, in which the holes serve for passages to reach the egg-patches, while the sateen, to some extent, prevents the egg-patches from being defiled by the faeces of the beetles. The egg-patches are transferred, with the eggs clinging to them, into a jar in which beforehand a thin layer of food has been brought for the coming young larvae.

In a temperature of 25° C. the hatching of the eggs takes about 8 or 10 days.

When from a culture a sufficient number of eggs had been gathered the egg-patches were still kept in the incubator 20 days after the last gathering. One is quite certain then that all the eggs capable of development have been hatched. The egg-patches are removed, some fresh food added in the larvae jar and this is left to itself in the incubator for some time.

Like the pupae, the eggs were gathered only once a week.

When a large number of beetles is kept together in one box, the harvest of eggs is often too small in proportion to the number of beetles. If those same beetles are distributed over a series of small pots, the harvest of eggs increases considerably.

This fact is illustrated by the following case.

In a box of 21×10 cm. were 88 beetles; from these were obtained respectively 131—148—181 and 121 eggs in the last 4 gatherings. After distributing these 88 beetles over 8 little pots, the next harvest of eggs increased to 468, the 2nd to 560 eggs, i.e. more than four times the last harvest of the preceding series.

7. *Mortality.*

The mortality among the eggs, larvae and pupae is as a rule considerable; low mortality figures are exceptions.

a. Among the eggs. In the 6 nutrition experiments mentioned on page 195 there were in each jar an equal number of eggs (viz. 300), all of the same origin. The difference between this figure and the number of young larvae (living + dead) which were counted at a definite point of time, denotes the number of not-hatched eggs.

To each 100 eggs laid out, the mortality in those 6 cultures amounted.

For N°.	1	to	16.6 %
„ „	2	„	41.3 „
„ „	3	„	17.3 „
„ „	4	„	34.3 „
„ „	5	„	24.6 „
On an average			28.2 %

The figures diverge rather much, whereas a special cause cannot be pointed out. At first arose the thought of errors in the counting which was carried out by spreading the bran very carefully, bit by bit.

The larvae were, indeed. counted only about a month after they had been transferred from the egg-patches to the food, and being very small, some might have been overlooked.

To verify this method of spreading, the egg-patches, in four other trials, were deposited in empty dishes (not provided with food), and the newly hatched larvae counted and removed. Any overlooking of the larvae was precluded in this manner. The result of these four experiments was as follows.

N°.	Eggs deposited.	Larvae obtained.	Not hatched eggs.	
			Total.	in %
1	75	65	10	13.3 %
2	117	105	12	10.2 „
3	191	136	55	28.7 „
4	108	75	33	30.5 „
Totals and mean	491	381	110	22.4 %

Here, too, there is little if any agreement among the mortality figures: The result of these experiments gave no occasion for giving up as unreliable the previous method of carefully spreading the bran in small quantities. This is why this proceeding has always been followed in the subsequent fixing of the mortality figures; also because one acquires such a dexterity in it that an overlooking of the larvae becomes all but impossible.

In the first two years the mortality of the eggs of nearly all cultures was determined. The following averages were then obtained.

Year of experiment.	Eggs deposited.	Larvae obtained.	Mortality of eggs.	
			Total.	in %
1915—1916	16451	11986	4465	27.1 %
1916—1917	66517	38861	27656	41.5 „
Totals and averages in the 2 years.	82968	50847	32121	38.7 %

The abnormally high mortality figure of the experimental year 1916—1917 as compared with 1915—1916, is striking. For this no definite cause can be assigned, except perhaps temperature influences,

as the harvest of the eggs of the year 1915—1916 took place in the spring and the summer, and that of the succeeding year in the autumn and the winter. The room was heated, it is true, and, with a single exception, the cultures were transferred into the incubator, but both the former and the latter were done only when the cold became unpleasant. In the experiment year 1917—1918 the winter was severe, with long continued frosty weather. The following experience was obtained.

A small series of cultures, which could not be accommodated in the incubator, stood free in the laboratory. In the daytime the room was heated, and during the frost it was heated slightly at night too, so that the minimum temperature was never below 7° C. This is known with perfect certainty as the temperature of the room and the incubators was regularly noted down 3 times a day. From these notes it appeared that the temperature in the early morning and late at night never sank below 7° C.

If one assumes, to be certain, that the temperature, at a given moment may have gone down to 5° C. before the thermometer indicated this sinking, it may be stated as a fact that this temperature is already deadly to the eggs. In the above-mentioned series of cultures the mortality was so high that only a few eggs were hatched.

From two jars, each of which contained 1250 eggs, not a single larva was got from one of them, and only two larvae from the other, even after the eggs, which still looked rather normal, had been kept in the incubator for a long time. This great sensitiveness of the eggs to low temperatures, was not further studied. On another occasion this circumstance will be reverted to. These observations have been recorded only to point out that the abnormal mortality of the year 1916—1917 may possibly be connected with temperature influences.

The 66517 eggs experimented on in that year were distributed over 5 series of 101 separate cultures in total.

In one series of 7 cultures 24500 eggs had been put, and in 4 series 42017 eggs in 94 cultures.

The average mortality of the first series with 7 cultures amounted to 53.7 %. For that of the 4 other series the figures were

2nd	series	of	7	cultures	8500	eggs	with	32.2 %	dead	
3rd	„	„	7	„	4661	„	„	38.4	„	„
4th	„	„	35	„	21472	„	„	37.7	„	„
5th	„	„	45	„	7384	„	„	25	„	„
Total			94	cultures	42017	eggs	with	34.4 %	dead.	

If one leaves the abnormal high mortality of 53.7 % of the first series out of consideration, the average egg mortality over the two experiment years of 58468 eggs becomes 32.4 %.

As the outcome one may therefore assume that, in general, only 2/3 of the number of eggs are hatched.

b. The mortality among the larvae.

As has been said, the cause of the egg mortality is still uncertain; that of the larvae mortality gives more positive indications. Fortunately epidemics have not appeared up till now. So they cannot have played a part in the mortality figures mentioned below. The larvae gnaw at each other's bodies and perhaps they sometimes eat each other up entirely; this cannibalism is, to be sure, the main cause of the larvae mortality.

A small percentage not gnawed at, died of unknown causes.

The larvae mortality in the experiments years 1915/1916 and 1916/1917 was:

Year of experiment.	Number of Larvae the culture was begun with	Dead Larvae.	Larvae Mortality in 100 larvae.
1915—1916	11986	3655	30.4 %
1916—1917	11294	1983	17.5 „
Totals and average.	23280	5638	24.2 %

Here the opposite case to that of the egg-mortality presents itself, viz. the first experiment year shows a considerably higher mortality figure than in the second year.

A factor that may have influenced this lies in the circumstance that an addition of thin fresh cut slices of potato or carrot scattered on the food (enhancing the humidity) had a specially favourable effect, not only on the growth and development of the larvae, but particularly on the mortality of the pupae. With regard to this, convincing figures will be submitted when the pupae mortality will be treated.

In consequence of the results obtained in the early part of 1917, the addition of slices of potato was started late, when a large part of the total number of pupae obtained of that experiment year had been already gathered. By this the late gathered pupae (together

with the larvae) profited by this addition, but, of course, not the pupae that had been then collected already. Hence the pupae-mortality of 1916/1917 is still very high and even higher than of 1915/1916. Now, the connection (alluded to above) that may exist between the mortality figures of larvae and pupae appears from the following. When one allows a number of counted larvae to pupate in a glass jar, and after some time adds the pupae gathered + the dead larvae + the remaining living larvae, the sum total is, as a rule, smaller than the number of larvae with which the culture was started. As an escaping of larvae from the glass jars does not occur (we never found any larvae crawling about in the incubator since the use of glass jars), the lacking larvae cannot but have been eaten up. This eating-up most probably took place not in the larval but in the pupal state, when the newly emerged body is still soft. The annihilation of these still soft pupae has then been executed in a much more radical manner than in the larvae gnawed at, while by the white colour the fragments of these pupae are much more difficult to find back than the relatively bigger remains of the brown larval bodies. This practically estimates the mortality figure of the larvae too high, and that of the pupae too low. This circumstance applies more specially to the year 1915/1916 than to 1916/1917, because in the latter year, as has been mentioned, a part of the larvae were already provided with slices of potato.

This expedient promoted the growth of the larvae and an earlier pupation, and strongly diminished the mutilation of the pupae; in consequence the figure of the larvae mortality (by the manner of fixing this figure) had then to decrease.

Now although these influences have, no doubt, asserted themselves, they were not of such a nature as to satisfactorily account for the great difference of the larvae mortality in these two years. Similar great differences appear also between the cultures (of one series) that have been exposed to equal exterior influences of food and temperature, and disagree only in one point, viz. in the time when the eggs were deposited, and in the number of these.

c. The mortality among the pupae.

The mortality among the pupae appears in the same way as among the larvae, viz. by gnawing-off, and by an unknown cause by which they dry up or, by way of rare exception, become black, and the body remains soft.

Besides these pupae eaten at, also others are found, not dead but wounded. The humour that has flowed from the wound is then

mixed with the bran and dried up into a lump. Such wounded pupae do not develop into beetles, but die sooner or later in proportion as the wound occurs on more or less vital organs.

The cause of these injuries is alike a beginning of gnawing by the larvae, from which the young pupa has been able to withdraw, as it always reacts to mechanic stimulation with vehement movements.

The gnawing away may, especially in young pupae, be so far advanced that only small remainders of the chitin-shell are found back.

Between these extremes one finds many intermediate stages of mutilation.

With this, the mortality among the pupae is not yet at an end. The pupa has still a critical period to pass through, viz. the time shortly before casting the pupal moult. Some unknown disturbance or other during the metamorphosis either occasions its death, or prevents a normal beetle from emerging.

The disturbance usually manifests itself in that the wings are defective, or are not perfectly developed, and that the pupal moult in the distal part of the body is not removed. The legs are mostly developed so far that these pseudo-beetles can utilize them yet. They are wretched animals, which crawl about needy and invalid, and die after a short time.

They have been mentioned separately as "half beetles" in ourmortality lists. The mortality of pupae gathered in the years 1915/1916—1916/1917 and 1917 is shown in the table below.

	Pupae gathered.	Of the pupae obtained died		Mortality of Pupae in %.		
		as pupae	as halfbeetles	as pupae	as halfbeetles	Total
1915—1916	8331	1269	150	15.2 %	1.8 %	17 %
1916—1917	28138	9355	1665	33.2 „	5.9 „	39 „
1917	8135	1617	201	19.8 „	2.4 „	22.3 „
Total and averages	44604	12241	2016	27.4 %	4.5 %	31.9 %

More than once already I had been struck by the fact that if I laid big pieces of rusk, soaked with water, in the larvae jar, the larvae greedily eat of them. This fact led me to the supposition

EXPERIMENT I.

Without slices.						*With* slices.					
Harvest.		Pupae gathered.			Deathrate to each 100 pupae gathered.	Harvest.		Pupae gathered.			Deathrate to each 100 pupae gathered.
N°.	Date 1917.	Living.	Dead.	Total.		N°.	Date 1917.	Living.	Dead.	Total.	
1st	10 January	54	36	90	40 %	1st	10 January	78	14	92	15.2 %
2nd	17 „	97	99	196	50.8 „	2nd	17 „	76	54	130	41.5 „
3rd	24 „	100	53	153	34.6 „	3rd	24 „	200	13	213	6.1 „
4th	30 „	44	24	68	35.2 „	4th	30 „	115	8	123	6.5 „
5th	6 February	70	41	111	36.9 „	5th	6 February	135	18	153	11.6 „
6th	13 „	71	32	103	31 „	6th	13 „	122	1	123	0.8 „
	Total and average.	436	285	721	39.5 %		Total and average.	726	108	834	12.9 %

EXPERIMENT II.

	20 February	199	60	259	22.1 %		20 February	280	6	286	2.1 %

that the mutilating of the pupae by the larvae was perhaps brought about by want of humidity, given the circumstance that the food in the incubator dried up more and more, until it got crumbly and was renewed.

I first put out a feeler by laying large thin slices of fresh beetroots on the top of the food in a few jars. The outcome was a surprise. The harvest from these jars provided with slices of beetroot was not only greater, but the eating of pupae had diminished in a striking way. Then the following course was taken.

Two jars were provided with fresh food. In each an equal quantity of larvae was put. One of these jars got 8 slices of beetroot or carrot, the other none. From these two jars 6 harvests of pupae were taken. The results are shown in the tabular scheme before and speak clearly enough.

One will see a considerable decrease of the deathrate in each harvest. The decrease is slightest in the 2nd and the 5th harvest. Now it appears from notes made, that in the periods between January 10 and 17 and between Jan. 30 and Febr. 6 i. e. between the 1st and 2nd and the 4th and 5th harvests no carrot had been added, because the bran still felt very humid to the touch from the previous time.

This after-effect of the humidity of the previous addition of slices is yet so great as to diminish the deathrate in both cases, in the 1st by 9 %, in the 2nd by 25 %.

This experiment was repeated on another quantity of larvae, of which in the two jars an equal number was again deposited. Here, too, the result was again in favour of the jar *with slices*, of which the mortality was 20 % less than in that *without* carrot (of Experiment II). It is also remarkable that in both experiments the total number of gathered pupae is larger, which clearly indicates that the growth of the larvae is very much furthered by the humidity.

I was not quite convinced and started a third trial.

I then reversed the state of humidity for the larvae at every turn after a number of harvests. Two jars were each provided with exactly 1000 larvae. In order to be sure that these larvae were in the same stage of development, they were weighed beforehand. The weights were the same for each group, viz. 110 grammes. The vessels got the same weight of food; one of them got 8 slices besides, the other none.

When the food in the jar *with slices* was consumed earlier than that in the other (which always occurred in all series of experi-

EXPERIMENT III*a*.

Without slices (1000 Larvae). (A)						
Harvest.		Pupae gathered.			Deathrate to each 100 Pupae gathered.	Dead Larvae.
N°.	Date 1917.	Living	Dead.	Total.		
1st	2 April	58	28	86	32.5 %	5
2nd	7 „	137	16	153	10.4 „	12
3rd	12 „	31	18	49	36.7 „	14
4th	17 „	11	12	23	52.1 „	1
5th	21 „	6	4	10	40 „	5
	Total and average.	243	78	321	24.2 %	37

With slices (1000 Larvae). (B)						
Harvest.		Pupae gathered.			Deathrate to each 100 Pupae gathered.	Dead Larvae.
N°.	Date 1917.	Living	Dead.	Total.		
1st	2 April	69	15	84	17.8 %	4
2nd	7 „	131	6	137	4.3 „	10
3rd	12 „	61	3	64	4.6 „	7
4th	17 „	33	2	35	5.7 „	6
5th	21 „	23	0	23	0 „	1
	Total and average.	317	26	343	7.5 %	28

ments and which fact should be particularly noted), both were provided with fresh food to keep the circumstances as equal as possible. Five days elapsed between two successive harvests; during all the time of the experiment the jars remained in the incubator.

The result of the first 5 harvests is shown in the table on page 212.

As the table shows, the average deathrate in the jar *without slices* was about 17 % higher than in the one *with slices*. The food was renewed twice, viz. on April 12 and 21. In both cases the food *with slices* had already become so crumbly that it had to be removed. Under ordinary circumstances, the renewal of the food of the other vessel (the one *without* slices) would not have been necessary. As has been said already, this case occurred repeatedly in all series experimented on. At the end of the 5th harvest the larvae were sieved and counted to verify all figures.

Jar A. Experiment III a. *without* slices)

Number of larvae the culture was started with	1000
on the sieve were left	642 larvae
living + dead pupae gathered	321 „
dead larvae	37 „
total	1000

Jar B. (Experiment III a *with* slices).

Number of larvae the culture was started with	1000
on the sieve were left	629 larvae
living + dead pupae gathered	343 „
dead larvae	28 „
total	1000

The subsequent series of harvests were dealt with as follows.

The slices of potato were added to those larvae that had never enjoyed them, i. e. to the 642 larvae of jar A. The 629 larvae of jar B, which had always had slices hitherto, had to do without this addition.

The figures of the harvest of this series are given in the table on the following page.

With the exception of the 1st and the 6th harvest the mortality figure for the jar *without slices* was considerably higher again in each successive harvest. That the 1st harvest should be an exception to it could not but be expected. The larvae had, indeed, in the former harvest, profited from humid surroundings, and the after-effect of this manifested itself in the next harvest in spite of the changed condition. The 5 % lower deathrate in the jar *without slices* does not therefore

EXPERIMENT III*b*.

629 Larvae originating from B. Experiment III*a*. *Without* slices. (A)						
Harvest.		Pupae gathered.			Deathrate to each 100 pupae gathered.	Dead Larvae.
N°.	Date 1917.	Living	Dead.	Total.		
1st	25 April	8	2	10	20 %	0
2nd	1 May	17	8	25	32 „	1
3rd	6 „	16	16	32	50 „	3
4th	11 „	13	6	19	31.5 „	7
5th	16 „	21	8	29	27.5 „	8
6th	21 „	27	5	32	15.6 „	1
7th	26 „	14	12	26	46.1 „	4
8th	31 „	8	5	13	38.4 „	1
9th	5 June	16	3	19	15.7 „	1
	Total and average.	140	65	205	31.7 %	26

642 Larvae originating from A. Experiment III*a*. *With* slices. (B)						
Harvest.		Pupae gathered.			Deathrate to each 100 pupae gathered.	Dead Larvae.
N°.	Date 1917.	Living	Dead.	Total.		
1st	25 April	6	2	8	25 %	0
2nd	1 May	19	2	21	9.5 „	4
3rd	6 „	28	0	28	0 „	1
4th	11 „	35	1	36	2.7 „	3
5th	16 „	24	1	25	4 „	0
6th	21 „	26	7	33	21.2 „	5
7th	26 „	12	1	13	7.7 „	6
8th	31 „	19	1	20	5 „	1
9th	5 June	24	1	25	4 „	2
	Total and average.	193	16	209	7.6 %	22

form an exception, but on the contrary, confirms the rule that the addition of slices caused a strong regression of the death rate of the pupae.

The exception of the 6th harvest had been brought about by the circumstance that in consequence of the excessive humidity in the jar *with* slices, the food had clotted and grown quite mouldy.

The wall of the jar was covered with big drops of water.

The 7 dead pupae gathered had not been gnawed at, indeed, but were black. Here the too much of a good thing, had apparently produced a reverse effect. The food of the jar under discussion had to be renewed for that reason, and this was done in both vessels, again for the sake of the uniformity of circumstances.

Notwithstanding these two exceptions the average mortality of the 9 harvests had fallen by 24 % for the jar *with slices* after all.

At the close of the 9th harvest of the above trial series III*b*, the larvae were sieved and counted to verify the figures obtained, with the following result:

Jar A. (Experiment III*b without slices*).

Number of larvae this series was started with . . .		629
On the sieve were left	398 larvae	
Living + dead pupae gathered . . .	205	
Dead larvae	26	
Total	629	

Jar B. (Experiment III*b with slices*).

Number of larvae this series was started with . . .		642
On the sieve were left	418 larvae	
Living + dead pupae gathered . . .	209	
Dead larvae	22	
Total		649
More individuals accounted for than there were at the outset		7

The verification of jar *B* shows an excess of 7 individuals.

How the error has arisen, is not known. As a rule such a verification shows a deficit, as the remains of a number of individuals are not found back. The mistake, however, if it has been made by inaccurate counting, cannot raise the deathrate, but rather lowers it, so that one need not care about it any further. For the 3rd harvest series the slice-food was again reversed.

The 418 slice-larvae of Jar B no longer got any slices; the 398 of jar A, which had not had any slices in the 2nd harvest series, were provided with them now. The result of this 3rd series, with a summary of the three series together is given on page 216

EXPERIMENT III *c*.

418 Larvae originating from B. Experiment III*b*. *Without* slices. (A)

Harvest.		Pupae gathered.			Deathrate to each 100 pupae gathered.	Daed Larvae.
N°.	Date 1917.	Living	Dead.	Total.		
1st	10 June	6	2	8	25 %	3
2nd	15 „	10	3	13	23 „	1
3rd	20 „	17	5	22	22.7 „	0
4th	25 „	12	5	17	29.4 „	0
5th	30 „	12	1	13	7.7 „	0
6th	5 July	5	2	7	28.5 „	0
	Total and average.	62	18	80	22.5 %	4
	Summary Experiment III, IV and V.					
	Experiment III*a*	243	78	321	24.2 %	37
	„ III*b*	140	65	205	31.7 „	26
	„ III*c*	62	18	80	22.5 „	4
	General total and average.	445	161	606	26.5 %	67

398 Larvae originating from A. Experiment III*a*. *With* slices. (B)

Harvest.		Pupae gathered.			Deathrate to each 100 pupae gathered.	Dead Larvae.
N°.	Date 1917.	Living.	Dead.	Total.		
1st	10 June	13	6	19	31.5 %	1
2nd	15 „	19	3	22	13.6 „	4
3rd	20 „	21	1	22	4.5 „	1
4th	25 „	15	0	15	0 „	2
5th	30 „	17	1	18	5.5 „	0
6th	5 July	9	0	9	0 „	3
	Total and average.	94	11	105	10.4 %	11
	Summary Experiment III, IV and V.					
	Experiment III	317	26	343	7.5 %	28
	„ IV	193	16	209	7.6 „	22
	„ V	94	11	105	10.4 „	11
	General total and average.	604	53	657	8 %	61

Without slices.					*With* slices.				
Number of the harvest	Dead pupae gathered			% mutilated in 100 dead pupae	Number of the harvest	Dead pupae gathered			% mutilated in 100 dead pupae
	Total dead	Uninjured	mutilated			Total dead	Uninjured	mutilated	
1st	28	11	17		1st	15	15	0	
2nd	16	5	11		2nd	6	6	0	
3rd	18	1	17		3rd	3	3	0	
4th	12	3	9		4th	2	2	0	
5th	4	1	3		5th	0	—	—	
Tot. and average.	78	21	57	73 %	Tot. and average.	26	26	0	none
6th	2	0	2		6th	2	2	0	
7th	8	2	6		7th	2	0	2	
8th	16	0	16		8th	0	—	—	
9th	6	1	5		9th	1	1	0	
10th	8	4	4		10th	1	1	0	
11th	5	2	3		11th	7	7	0	
12th	12	0	12		12th	1	1	0	
13th	5	2	3		13th	1	1	0	
14th	3	1	2		14th	1	1	0	
Tot. and average.	65	12	53	81.5 %	Tot. and average.	16	14	2	12.5 %
15th	2	1	1		15th	6	3	3	
16th	3	1	2		16th	3	1	2	
17th	5	0	5		17th	1	0	1	
18th	5	1	4		18th	0	—	—	
19th	1	0	1		19th	1	1	0	
20th	2	1	1		20th	0	—	—	
Tot. and average.	18	4	14	77.7 %	Tot. and average.	11	5	6	54.5 %
Gener. tot. and average.	161	37	124	77 %	Gener. tot. and average.	53	45	8	15 %

Here too, the after-effect in the 1st. harvest is again clearly observed. Properly speaking, it might be expected that this after-effect should be continued in a few harvests more, as the slice-larvae, after the 2nd harvest series, looked so much bigger and more vigorous than those of the dry jar. As a matter of fact the longer duration of the after-effect under discussion (in this as well as in the previous trial series) clearly finds expression in the circumstance that the differences of the deathrates between the two trial jars ever increase up to the 4th harvest. So, if as a final result it is stated that the mortality figure in the slice-jar has fallen by 18.5 %, this figure is certainly not flattered, but estimated too low, a good deal too low if one considers carefully the figures and the circumstances under which they were obtained.

The supposition mentioned on page 211 that the gnawing of the pupae might be a consequence of the larvae's need of humidity is corroborated by comparing the numbers of dead pupae mutilated or not, harvested from the two jars.

From the table on the former page it is seen that in the jar *without* slices 77 % of the dead pupae were eaten at, and by far most of them very strongly, whereas in the slice-jar this figure was only 15 % and even then so slightly that often doubt arose as to whether or not they had to be noted down as "eaten at".

The determination of the average mortality among the eggs, larvae, and pupae was to me of this practical signification that once I knew this, the approximate quantity of eggs for a given culture could be fixed, in order to get at my disposal a desired number of beetles. The outlay of too large a number of eggs was a needless labour and waste of time, leaving apart the drawbacks connected with it.

The labour spent on the fixing of these figures in the first three years of experiment, has been amply rewarded by the use made of them. The average deathrate of eggs + larvae + pupae to each 100 eggs laid out amounts to the considerable figure of about 58 %.

LITERATURE.

1. Brehm. Tierleben. Insekten.

2. Frenzel. Ueber Bau und Thätigkeit des Verdauungskanals der Larve des Tenebrio molitor Berl. Entom. Zeitsch. Bd. XXVI. 1882.

3. Frisch, J. L. Beschreibung von allerlei Ins. in Deutschland 1720.

4. Saling, Th. Zur Kenntnis der Entwickelung der Keimdrüsen von Tenebrio molitor. Inaugural Dissert. Marburg 1906.

5. Sturm, Jakob. Deutschlands Fauna in Abbildungen uud Beschreibungen. V. Insekten. Käfer.

Utrecht, February 1920.